A STUDY OF THE RATE OF DISSOLUTION OF MAGNESIUM IN ACIDS

by

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ABSTRACT

A brief critical account is given of Nernst's theory of heterogeneous reactions and of the modifications to it that have been proposed by various investigators. This is followed by a summary of the work done by a number of workers with ultrasound in the study of heterogeneous chemical and electrochemical reactions between solids and liquids.

In Section II, an account is given of the experimental techniques used in the present work and of the methods of expressing the results. The experimental work carried out by the present author on the reaction between magnesium and hydrochloric acid, and between magnesium and a number of other acids, is described and detailed results reported.

Section III is devoted to discussions of methods of effecting a change of control in heterogeneous reactions, to considerations of problems involved in determining chemical rate constants for partly diffusion controlled heterogeneous reactions, and to the mathematical treatment of rate equations for reactions where the apparent area of a dissolving magnesium cylinder changes appreciably during the course of reaction.

In Section IV, the experimental results are discussed in detail, and it is shown that the data for the acids investigated in this work do not fit a Brönsted-Pedersen relationship. Possible reasons for this are examined in detail. Finally, some interesting theories of heterogeneous reactions between solids and liquid reagents are briefly discussed.

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SECTION I

Introduction

The view that the observed rates of chemical reactions between solids and liquid solutions can be controlled by transport processes, i.e. mass transfer of ions or molecules by convection and diffusion, is not a recent one. Thus W. Nernst[1], in 1904, promulgated his general diffusion theory of the kinetics of heterogeneous chemical reactions between solids and liquids according to which the rate of reaction between a solid and a dissolved substance is controlled by the speed with which solute species can diffuse through a thin static layer of solution, of thickness δ, adhering to the surface. Most prominent among the workers who adopted Nernst's view point were L. Brunner[2]. K. Jablczynski and St.Jablonski[3], and R.G. Van Name and his co-workers[4] who soon produced experimental evidence in support of the diffusion layer theory. On the other hand, other workers, notably T. Ericson-Auren and W. Palmaer[5], M. Wildermann[6], Von E.N. Gapon[7], S. Miyamoto[8], P.S. Roller[9] and E.A. Moelwyn-Hughes[10], have criticised the theory, sometimes even to the extent of denying the existence of a diffusion layer at the solid-liquid interface.

Nernst and Brunner supposed that the diffusion layer theory was generally applicable to heterogeneous reactions between solids and liquid reagents. However, it was soon pointed out by Van Name and D.V. Hill[11] that three types of heterogeneous reactions between solids and liquids were possible:

(a) The chemical reaction at the solid surface is very much faster than the rate of diffusion of the solute to the interface, with the consequence that the observed rate is controlled by the latter. In this case, a concentration gradient of solute would be set up at the interface and Fick's first law of diffusion could be applied in order to derive a rate equation for the reaction.

(b) The chemical reaction on the solid surface is much slower than the rate of diffusion, so the rate-determining process is the former. In such reactions there is no concentration gradient at the surface of the solid and there is a uniform concentration of solute throughout the liquid phase.

(c) The rate constants for the diffusion and chemical processes are of comparable magnitude, and the rate of transport of solute molecules to the solid surface is equal to the rate at which they are consumed by the chemical reaction. In this type of heterogeneous reaction (the so-called intermediate type) there is a concentration gradient at the solid-liquid interface, but the concentration of reactive solute at the surface of the reacting solid is not zero.

On general kinetic grounds, there is no sharp distinction between the possible types of heterogeneous reaction system and in practice a gradation between the limiting cases of activation-and transport-control is encountered, Van Name and Hill's class (c) being the general case.

Concrete examples of reactions conforming to Van Name and Hill's classification are as follows:- (i) the reaction between a copper cylinder rotating at 6,400 r.p.m. and 0.1 M acetic acid buffered by 0.1 M sodium acetate in the presence of thionine as a depolariser studied by M. Hochberg and C.V. King[12] is an example of a chemically controlled heterogeneous reaction; (ii) the reaction between cadmium discs 3.83 cm in diameter rotating at 200 r.p.m. and 0.02 M iodine dissolved in aqueous 0.5 M KI studied by Van Name[4d] and co-workers is an example of a diffusion controlled reaction; to Van Name and Hill's class (c) belongs the reaction between copper cylinders rotating at 3,200 rp.m. and 0.1 M acetic acid buffered by 0.1 M sodium acetate, in the presence of 3.5×10^{-3} M p-benzoquinone as depolariser, studied by M. Hochberg and C.V. King[12].

Although Nernst's assumption of a stationary diffusion layer at the solid-liquid interface of a system subject to diffusion control is now generally held to be invalid, many workers[13] in the field of heterogeneous reactions nevertheless adhere to a modified version of Nernst's view in which a static layer has been replaced by a hydrodynamic layer in which mass transfer occurs by both diffusion and convection. In this connection, it is pertinent to inquire whether there is any direct experimental evidence for the existence of boundary layers at solid-liquid interfaces in heterogeneous reactions. As a matter of fact, there is strong evidence in support of their existence in certain systems:

(i) C.V. King and S. Brodie[14] found that a thin layer of solution at the surface of a barium hydroxide crystal in a rapidly stirred solution of dilute acid containing phenolphthalein became pink.

(ii) H.F. Walton[15], when discussing his own work and that of P.A. Jacquet[16] on the electrolytic polishing of copper, mentions the fact that a thin, viscous layer of solution, rich in copper salts, is seen to form on the surface of a copper anode immersed in acidified copper Phosphate solutions.

(iii) A Brenner[17] has used a freezing out method to demonstrate the existence of a diffusion layer and to measure its thickness, which was found to be of the expected order of magnitude (about 10^{-3} cm).

(iv) The Schlieren interferometer method[18] has been used to render diffusion layers visible and to evaluate δ, the thickness of the layer.

(v) H.J. Antweiler[19] has photographed the diffusion layer at the dropping mercury cathode.

In order to give an orderly and balanced account of the work that has been done in the field of heterogeneous reactions involving solids and liquid reagents, it is necessary to discuss Nernst's theory in some detail before the more modern hydrodynamical treatments of such reactions are considered.

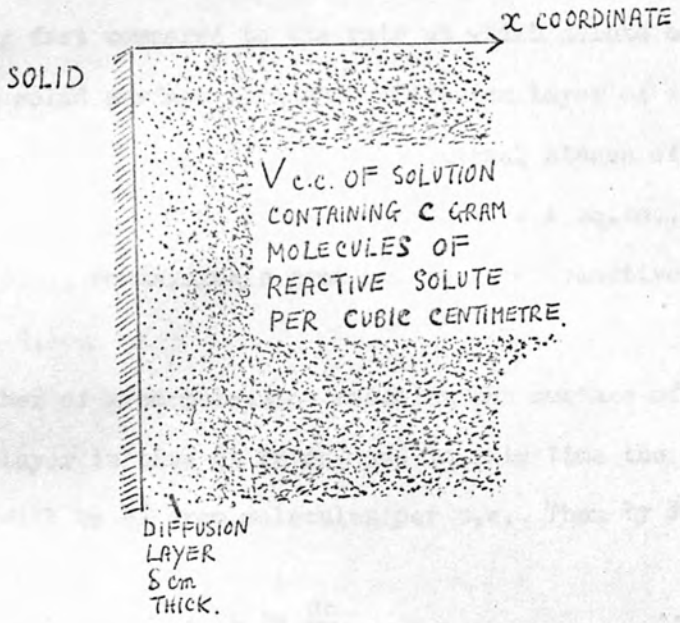

x COORDINATE
SOLID
V c.c. OF SOLUTION
CONTAINING C GRAM
MOLECULES OF
REACTIVE SOLUTE
PER CUBIC CENTIMETRE.
DIFFUSION
LAYER
δ cm
THICK.

Figure 1

Nernst assumed that chemical reactions at the interface were invariably very fast compared to the rate at which solute molecules could diffuse to the solid surface through a diffusion layer of thickness δ cm., formed by reaction products in the initial stages of reaction.

Let the area of solid exposed to attack be A sq.cm., and the volume of solution V c.c., containing c gram molecules of reactive solute per c.c. (see Fig. 1.).

The number of gram-molecules reaching the surface of solid through the diffusion layer in time dt is dn, and in this time the fall in concentration will be $\frac{dn}{V}$ gram molecules per c.c. Then by Fick's first law of diffusion,

$$\frac{dn}{dt} = - DA \frac{dc}{dx} \qquad \ldots\ldots \quad (1),$$

where D is the diffusion coefficient of the solute and $\frac{dc}{dx}$ the concentration gradient normal to the surface.

Now $cV = n$, so $Vdc = dn$ and $\frac{dn}{dt} = V\frac{dc}{dt}$.

Hence equation (1) becomes: $V\frac{dc}{dt} = - DA\frac{dc}{dx}$

$$\therefore \quad \frac{dc}{dt} = - \frac{DA}{V} \frac{dc}{dx} \qquad \ldots\ldots \quad (2)$$

Nernst assumed that the concentration gradient is given by $\frac{c - c_s}{\delta}$, where c_s is the solute concentration at the surface.
Substitution in (2) gives:

$$- \frac{dc}{dt} = \frac{DA}{V\delta} (c - c_s) \qquad \ldots\ldots \quad (3)$$

A further assumption made by Nernst was that for many reactions, e.g., those between metals and acids, c_s is virtually zero, so equation (3) simplifies to:

$$- \frac{dc}{dt} = \frac{DA}{V\delta} c \qquad \ldots\ldots \quad (4)$$

which is an equation of the first order in solute concentration.

The first order constant is given by

$$k = \frac{DA}{V\delta} \qquad \ldots\ldots \quad (5)$$

From equation (5), $\delta = \frac{DA}{Vk}$, so the thickness of the diffusion layer can be calculated from the observed first order velocity constant and the diffusion coefficient of the solute.

This theory was soon put to the test by Brunner[2], who determined the thickness of the Nernst diffusion layer for a number of different heterogeneous reactions. It is significant that these values are all of the same order of magnitude, a mean value being about 3×10^{-3} cm at 20°C. Although Moelwyn-Hughes[10] points out that such a value for the thickness of the diffusion layer is improbably large, the fact that δ has about the same value for many reactions of varying chemical character strongly suggests that the rates are controlled by a transport process.

The thickness of the diffusion layer should decrease as the rate of stirring increases, with the consequence that the rate of reaction will increase. This offers the possibility of another test of the theory. Indeed, many workers have found by experiment that there is a power relationship between rate constant and speed of revolution, of the form $k_T \propto r^s$, where k_T is the observed rate constant per unit area at unit volume, r = the number of revolutions per minute, and s is the 'stirring coefficient'. The values of s determined by a number of workers for a wide variety of heterogeneous chemical reactions range from 0.42 (W. Nernst and E.S. Merriam[20]) to 1 (e.g. C.V. King and M. Schack[21], R.S. Johnson and H.J. McDonald,[22] K. Nagel and T. Renner[23]).

It is evident from equation (4) that a number of different solids should dissolve at the same rate in the same solution under the same experimental conditions

(such as temperature, type and rate of stirring, similar reaction vessels) provided the solids are insoluble in the solvent and that the observed rates are transport-controlled. Van Name[4] and his collaborators found that, within the limits of their experimental errors, the metals cadmium, cobalt, copper, iron, mercury, nickel and zinc dissolved in aqueous iodine solutions at the same rate, and this was later confirmed by A.C. Riddiford and L.L. Bircumshaw[24]. Nernst explicitly assumed that δ is a function of the rate of stirring and of the geometry of the system only, and is independent of the coefficient of diffusion of the solute, of the viscosity of the solution, and of the temperature. He reasoned that if δ is experimentally determined for one solid-liquid system with a given type and rate of stirring, then the rate constant k_T can be calculated for other heterogeneous solid-liquid reactions occurring under the same flow conditions. Brunner[2] determined δ from his measurements of the dissolution rates of benzoic acid in water, then calculated by means of equation (4) the rates of dissolution of magnesium oxide in various acids, making use of the known coefficients of diffusion. The agreement between calculated and observed rates was found to be reasonable.

It has been found experimentally that an inverse relationship holds between the viscosity η of a medium and the diffusion coefficient D of the solute; thus $D\eta$ = constant. From equation (5), $k_T = \frac{D}{\delta}$. Combining these two relationships, it is seen that k_T will be inversely proportional to the viscosity of the medium, provided δ is a function of the type and rate of stirring only. C.V. King and M.M. Braverman[25] measured the effect on the rate of dissolution of zinc obtained by changing the viscosity of a hydrochloric acid solution by adding sucrose, ethyl alcohol and a number of salts. They found on plotting rate versus $\frac{30}{\eta}$ that the inverse proportionality holds rather well. Furthermore,

they claim that Van Name and Hill's[4] results on the effect of alcohol up to 3 M and sucrose up to 1 M on the rate of dissolution of cadmium in iodine-potassium iodide solutions, when plotted in the same way, give a similar inverse relationship, thus lending further support to the Nernst theory.

If δ is a function of the rate and type of stirring only, k_T and D should have the same temperature coefficient, and hence the observed critical increment should be about 4,300 calories at 25°C[10]. It has been found that many heterogeneous reactions do have about this value for the observed critical increment, e.g., Van Name and Hill[4] found that E_A = 4,000 calories per mole for the dissolution of cadmium in aqueous iodine. However, it must be pointed out that some homogeneous reactions in solution have a critical increment of this order, or less, so that mere observation of such an activation energy is not in itself evidence for the occurrence of a diffusion-controlled reaction.

The defects of the Nernst theory must now be considered. As previously stated, the possibility of wholly chemically-controlled or partly chemically-controlled reactions was realised by Van Name and Hill. It was subsequently shown by several workers that the rates of some heterogeneous processes are activation controlled, e.g. M. Centnerszwer and W. Zablocki[26] found that the rates of dissolution of certain metals in acids are unaffected by the rate of stirring; Moelwyn-Hughes[10], discussing the kinetics of the decomposition of sodium hypochlorite in aqueous solution catalysed by suspensions of cobalt peroxide studied by O.R. Howell[27], points out that the observed critical increment of 16,600 calories per mole is far too high for a diffusion-controlled reaction and he explains the kinetics adequately on the assumption that the rate is controlled by activated collisions between hypochlorite ions and catalyst surface.

Re Nernst's assumption that the diffusion layer is stationary with respect to the solid surface, strong evidence in favour of the view that fluid motion persists down to the surface itself has been adduced by Roller[9], and by A. Fage and H.C.H. Townend[28]. The latter two investigators studied the turbulent flow of water in pipes with the aid of an ultramicroscope, and found that near the pipe wall the flow was laminar; motions of intensely illuminated particles in the laminae being observed to within a distance of 0.6×10^{-4} cm. from the wall. This distance in only 1/50 of the thickness (3×10^{-3} cm) of the so-called Nernst diffusion layer.

A theoretical treatment in terms of hydrodynamic principles for the case of a plane disc electrode rotating about an axis perpendicular to its plane has been given by B. Levich[29]. This treatment shows that a non-linear concentration gradient exists at the interface and that this gradient extends over a distance δ' from the solid surface into the solution. δ' is related to δ, the thickness of the hypothetical Nernst layer by

$$\delta = [0.8934 + 0.316 (\frac{D}{\nu})^{0.36}] \delta' \qquad \ldots\ldots (6)$$

where D is the diffusion coefficient of the solute and ν the kinematic viscosity of the solution ($\nu = \frac{\text{viscosity}}{\text{density}}$). In aqueous solutions at ordinary temperatures $\frac{D}{\nu} \doteq 10^{-3}$, so that equation (6) reduces to,

$$\delta = 0.894 \delta' \qquad \ldots\ldots (7)$$

Finally, Nernst's assumption that δ is independent of the diffusion coefficient of solute, the viscosity of the medium, and the temperature must be examined. From the relationship $k_T = \frac{D}{\delta}$, k_T should be proportional to D, provided δ is independent of D. However, experiments by C.V. King and W.H. Cathcart[30], and by Eucken[31], have shown that k_T

is not directly proportional to D, but that a power relation exists between them, $k_T \propto D^p$. For the dissolution of magnesium cylinders in acids, King and Cathcart obtained the value p = 0.7, while A. Eucken found p = 0.66 for laminar flow. These results suggest at once that δ is a function of the diffusion coefficient of the solute, the viscosity of the medium (also suggested by the fact that viscous laminar flow occurs within the Nernst layer), and the temperature. Hence of course the temperature coefficients for k_T and γ need not be identical.

Thus in the face of the experimental evidence of Fage and Townend, and others, it appears that the concept of a stationary diffusion layer adjacent to the solid surface has to be abandoned. The investigations of Levich, and others, have shown that in these systems the rates of which appear to be governed by transport porcesses (where the observed rate is a function of stirring speed, etc.) there exists a concentration gradient extending from the solid surface to points in the liquid distant about δ from the surface. The experimental evidence for the existence of such a boundary layer in certain systems has already been outlined. In the case of laminar flow parallel to the solid surface, mass transfer will be partly by convection and partly by diffusion, the latter becoming more important as the surface is approached. For turbulent flow, such as is often encountered in systems of chemical interest, mass transfer from the body of the fluid to the boundary layer takes place by forced convection, while mass transfer across the boundary layer takes place by diffusion and by convection.

In general the quantitative treatment of mass transfer in heterogeneous systems is very difficult. Apart from the complex geometry of many systems, interfaces other than the ones where the actual chemical reaction(s) occur may influence the hydrodynamic flow patterns to a considerable degree, e.g., interfaces at the walls of a containing vessel,

or between a stirrer and liquid. However, theoretical treatments have been given for certain fairly simple geometrical systems, namely a rotating disc[29] and a rotating cylinder[32].

Any complete hydrodynamic treatment of mass transfer must take into account both the diffusive transport and the convective transport of matter. The rate of change with time of the concentration c of solute at a given point in a solution is given by the equation:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) - \left(u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z}\right) \quad \ldots\ldots \quad (8)$$

where u, v, and w are the velocity components of flow parallel to the x, y, and z axes, respectively, and D is the diffusion coefficient of the solute. The velocity components must be determined by the equations of continuity and by the Navier-Stokes equations, together with the appropriate boundary conditions. In cylindrical polar coordinates, equation (8) becomes:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{1}{r^2}\frac{\partial^2 c}{\partial \phi^2} + \frac{\partial^2 c}{\partial y^2}\right) - \left(v_r\frac{\partial c}{\partial r} + \frac{v_\phi}{r}\frac{\partial c}{\partial \phi} + v_y\frac{\partial c}{\partial y}\right) \quad \ldots\ldots \quad (9)$$

for which the origin of coordinates, in the case of a rotating disc, is the centr of the disc, and the y coordinate is the line through the origin perpendicular to the plane of the disc. The solutions of the equations of fluid motion applicable to simple systems have been obtained by T. von Karman[33] and W.G. Cochran[34], and Levich made use of the results to solve equation (9) for the ideal case of a large disc rotating in an infinite volume of solution under non-turbulent flow conditions. Levich assumed that c is independent of r, so that terms involving $\frac{\partial c}{\partial r}$ and $\frac{\partial^2 c}{\partial r^2}$ vanish from equation 9. For the steady state of

convective transfer, $\frac{\partial c}{\partial t} = 0$. The axial symmetry of the system makes it evident that the concentration c is independent of the angle ϕ. Hence the terms in ϕ disappear from equation (9) and it reduces to;

$$D \frac{d^2c}{dy^2} = v_y \frac{dc}{dy} \qquad \ldots\ldots (10),$$

which is readily solved.

The solution of equation (10) can be applied to a system of finite size, provided the diameter of the disc is $>> \delta$ and that the volume V of solution is large enough to reduce the hydrodynamic effects of the vessel walls to a minimum. As already mentioned, Levich found that $\delta = 0.894\delta'$, so that equation (3) becomes,

$$- \frac{dc}{dt} = \frac{DA}{V} \frac{(c - c_s)}{0.894\delta'} \qquad \ldots\ldots (11)$$

He also found from the solution of equation (10) that

$$\delta' = 1.805 \left(\frac{D}{y}\right)^{\frac{1}{3}} \left(\frac{v}{w}\right)^{\frac{1}{2}} \qquad \ldots\ldots (12),$$

where v = kinematic viscosity, w = angular velocity of the disc, and D = the diffusion coefficient of the solute. Hence,

$$\delta = 0.894\delta' = 1.612\, D^{\frac{1}{3}} y^{\frac{1}{6}} w^{-\frac{1}{2}} \qquad \ldots\ldots (13),$$

an important equation which relates the thickness of the Nernst diffusion layer (as calculated from equation (5)) to the diffusion coefficient of solute, the kinematic viscosity of solution, and the speed of rotation of the disc. Also it is readily seen that

$$k_T = 0.62\, D^{\frac{2}{3}} y^{-\frac{1}{6}} w^{\frac{1}{2}} \qquad \ldots\ldots (14).$$

From equations (11) and (13), it is seen that the rate of reaction $(- \frac{dc}{dt})$ should interalia be proportional to $w^{\frac{1}{2}}$. V.G. Siver and B.N. Kabanov[35] studied the limiting currents at an amalgamated copper disc cathode in

various solutions and in each case found that the limiting current was proportional to the square root of the angular velocity of the disc. Riddiford and Bircumshaw[24], studying the dissolution of zinc in I_2-KI solutions in the speed range 5-21 radians per second and using thin metal sheets rotated on a glass holder, found equation (14) to hold fairly well. D.P. Gregory and A.C. Riddiford[36] studied the same reaction, but used carefully prepared zinc discs 5.3 cm. in diameter in the speed range 73-292 r.p.m., at temperatures 20°-45°C. They found excellent agreement with the corrected equation. Both Siver and Kabanov, and Bircumshaw and Riddiford compared values of δ calculated from equation (13) with those experimentally determined by equation (5) of the simple Nernst theory, and found the agreement to be satisfactory, particularly at the higher rates of stirring.

Levich has also treated the case of laminar flow along a flat plate and has shown that,

$$\delta = 3 x^{\frac{1}{2}} D^{\frac{1}{3}} \nu^{\frac{1}{6}} U^{-\frac{1}{2}} \qquad \ldots\ldots \quad (15)$$

provided that the dimensions of the system are such that wall and edge effects can be neglected. Here x is the distance from the edge of the plate measured parallel to the surface of the plate and U is the characteristic velocity of the fluid. Thus the thickness of the diffusion layer increases with the distance from the edge of the plate. This is to be contrasted with the case of the rotating disc in a large volume of fluid in which the thickness of the diffusion layer is constant over all the disc surface. Thus, from theoretical considerations the thickness of the diffusion layer in any system depends among other factors upon the geometry of the system. It is a reasonable supposition to make that, in general,

under turbulent or non-turbulent conditions, δ (and δ') may be expressed as a function of D, ν, and the characteristic velocity U of the system. As D is an inverse function of ν, the small values of the powers on D and ν (equations (13) and (15)) explain why similar values of δ are frequently obtained for reactions of very different chemical character under the same flow conditions.

The complexity of the hydrodynamics of the processes of mass transfer in chemical reaction vessels, particularly when the interface is in motion, renders the quantitative treatment of heterogeneous reactions under turbulent conditions of flow very difficult (see, for example, Bircumshaw and Riddiford[13a], and V.G. Levich[37]. Dimensional analysis has proved to be of some value[38] for such systems. Such analysis yields the following relationship between δ and the dimensionless groups known as the Reynolds number (Rd) and the Prandtl number (Pr):

$$\delta = \left(\frac{l}{B}\right) (Rd)^{-a} (Pr)^{-b} \qquad \ldots\ldots \quad (16),$$

where l is the characteristic length (such as diameter of cylinder), B is a number, a and b are exponents. B, a and b must be determined by experiment. Neither (Rd) nor (Pr) involves Δc (change in concentration), so equation (16) leads to the important result that δ (and δ') is independent of the concentration difference at the interface. The exponent a is the stirring coefficient previously referred to and, as we have seen, has values ranging from about 0.4 to 1. Riddiford and Bircumshaw[13a] regard exponent b as having the constant value 0.33. Therefore, bearing in mind the definitions of (Rd) and (Pr), an examination of equation (16) shows that the powers on ν and D will have positive, fractional values and thus also indicates why similar values of δ are obtained for many chemical reactions of different character under the same flow conditions.

We have seen how the original Nernst theory has had to be modified in the light of the more modern hydrodynamic treatment of solid-liquid heterogeneous reactions, and how Fage and Townend's[28] observations on laminar flow at a solid-liquid interface gave experimental support to the findings of the hydrodynamic treatment concerning the nature of the diffusion layer. Moreover, we have listed various pieces of experimental evidence supporting the existance of diffusion layers in certain systems. Thus it seems that in many systems of chemical interest, convective-diffusive mass transfer can play an important part in determining the kinetic course of reactions. It is accordingly of the greatest importance to be able to apply practical criteria which will enable one to recognise heterogeneous reactions the rates of which are partly or wholly controlled by convective-diffusive mass transfer. Five such criteria have in general been applied by investigators in this field of reaction kinetics:

(i) Various solids dissolve in the same reagent at the same rate under the same flow conditions.

(ii) For a given solid dissolving in different reagents, the observed rates generally follow the diffusion coefficients of the reagents.

(iii) Usually the observed rate is nearly inversely proportional to the viscosity of the solution.

(iv) Stirring (forced convection) has a marked effect on the observed rates of diffusion controlled reactions.

(v) The temperature coefficients of diffusion controlled reactions are usually in the range 1.1 to 1.5 per $10^{\circ}C$ rise in temperature, whereas chemical reaction rate constants often have temperature coefficients of about 2. These coefficients apply, of course, to near-room-temperature conditions.

Mass transfer processes, when they control the overall rates of heterogeneous chemical reactions, hinder the elucidation of the true mechanisms of the reactions taking place on the surface of the solids, for the actual observed rates in such systems will be those of convection-diffusion, not of the chemical reactions. This appears to have been so in the case of some studies on the reactions of the metals magnesium and zinc with various acids. Thus M. Kilpatrick and H. Rushton[39] made an extensive investigation of the reactions of these two metals with aqueous solutions of a variety of strong and weak acids, with a view to testing the extended theory of acids and bases, and used their experimentally determined rate constants in a log k_A versus log K_A plot, where k_A was supposed to be the chemical rate constant for the reaction between the acid A and the metal, and K_A is the dissociation constant of the acid. As King and Cathcart[30] later pointed out, the reactions investigated by Kilpatrick and Rushton are diffusion controlled because the observed rates are markedly influenced by the rate of stirring of the solutions and by their viscosities. Moreover the low values of the temperature coefficients for the reactions between zinc and both hydrochloric and acetic acids found by King and Braverman[25] support their contention that these reactions are diffusion controlled. It therefore appears that the k_A values used by Kilpatrick and Rushton were not true chemical constants.

The initial purpose of the present investigation was two-fold: (a) to determine to what extent diffusion-convection processes control the rates of heterogeneous reactions between metals and various solutions, mainly acids; (b) to gain information relevant to the mechanism(s) of the chemical reactions at the surface of the metals.

With regard to (a), ultrasonic waves are used in an attempt to remove any diffusion layer that may be present at the metal-liquid interface, so that the reaction rate will then be controlled by the chemical processes occurring at the metal surface. Therefore by comparing the kinetics of reactions when they are influenced by ultrasound with the kinetics of the same reactions when they are not subjected to ultrasonic waves, one might determine to what extent convection-diffusion processes influence the rates of heterogeneous reactions.

Concerning (b), it could well be that the study of heterogeneous reactions influenced by ultrasound may provide information about the mechanism(s) of reactions between metals and acids, and therefore help to elucidate the nature of acids.

Ultrasonic waves have been used in a limited number of investigations of heterogeneous reactions involving solid-liquid interfaces. As early as 1933, N. Moriguchi[40] investigated the effect of ultrasonic waves of frequency $\doteqdot$ 470,000 c.p.s. on the rates of the reactions between zinc and hydrochloric or sulphuric acids, and between marble and hydrochloric acid. He used acid of strength 1.7 N and irradiated the heterogeneous systems intermittently with ultrasound. In each case he investigated, the ultrasound produced an increase in reaction rate (followed by observing the volume of gas evolved) of between four and five fold. He later[41] extended his investigations to include a study of the influence of ultrasonic waves on concentration polarisation in the case of copper electrodes dipping into 0.1 N copper sulphate solutions. From his results, which he plotted on a current density versus voltage graph, he concluded that within the limits of his experiments, ultrasonic waves could remove completely the diffusion layer on his copper wire electrode.

Other workers have later studied the effects of ultrasound on concentration gradients, notably in the field of electrochemistry.

E. Yeager and F. Hovorka[42] studied the effect of ultrasonic waves on the electrodeposition of copper, using frequencies of 200 and 1,000kc.p.s. at an intensity of 1 watt per sq.cm. They concluded that "the ultrasonic waves seem to remove completely these concentration gradients at reasonable current densities, particularly when gaseous cavitation bubbles are evident". A few years later, F. Hovorka, R. Penn and E. Yeager[43] used the Schlieren technique to study the effects of both standing and progressive ultrasonic waves on concentration gradients produced by electrochemical methods. They used 0.5 M copper sulphate solutions at a temperature of 25°C. With standing waves of frequency 500 kc.p.s. at intensities below cavitation levels, zones of depleted electrolyte at the cathode were observed to stratify at the displacement nodes while zones of excess electrolyte at the anode were observed to stratify at the displacement loops. The current density was about 85 millamps per sq.cm. The frequency of the progressive waves used by Hovorka, Penn and Yeager was about 1,000 kc.p.s. at an intensity of 5 watts per sq.cm. The electrolyte was 0.5 M copper sulphate solution and the current density used in the electrolysis experiments was about 65 milliamps per sq.cm., at a temperature of 25°C. Under these conditions, cavitation was produced in the electrolyte. The authors concluded that the effective thickness of the boundary layer at the cathode is reduced from 10^{-2} cm. with natural convection to 10^{-3} cm. with ultrasonic waves as well as with ordinary stirring, but that ultrasonic waves "are somewhat more effective in disrupting the boundary layer than vigorous conventional forced convection under the conditions involved in the present experiments". They are, however, careful to point out that the quantitative significance of their data should not be over-emphasised since the resolution of the Schlieren microscope is seriously limited by optical diffraction effects and "probably not much better than 10^{-3} cm".

The disruption of concentration gradients probably involves three factors: (i) acoustic streaming in the bulk of the solution; (ii) radiation pressure and other second order interactions with the concentration gradient; (iii) cavitation effects. Hovorka, Penn and Yeager consider cavitation effects to be most important in effecting the disruption of concentration gradients.

Recently, W.E. Rowe, and W.L. Nyborg[44] have studied the effect of localised sound on an electrode reaction and they observed that the rate of the reaction increased appreciably under the influence of the ultrasonic vibrations. They are of the opinion that the ultrasonic vibrations in their experimental system cause a decrease in the average thickness of the diffusion-convection layer at the electrode-electrolyte interface, so that the rate of reaction is increased.

A.A. Baram and O.A. Kokushkin[45] have recently studied the effect of comparatively low frequency (22 kc.p.s.) ultrasonic waves on the dissolution of small cylindrical tablets of benzoic acid in distilled water. They found that the dissolution of the acid was accelerated considerably more by the continous action of ultrasound than by mechanical stirring effected by rotating from three to five tablets on a special rod rotating at 400 rp.m. in 450 c.c. of distilled water. The dissolution rate increased approximately eightfold. Baram and Kokushkin also found that the rates of dissolution of the acid in the vibration nodes and antinodes of the standing ultrasonic wave system which they used are virtually equal. They conclude that the intensification of mass transfer processes under these conditions is due to the formation of small scale hydrodynamic streams of high velocities which cause the convective-diffusion layer at the interface to become very turbulent, and thereby increase the number of pulsations penetrating to the surface of the solid. It is noteworthy that several investigators[46] have observed intense microstreams of liquid media at the solid-liquid interface.

SECTION II

Practical Section

II(a) Preliminary Work on the Reaction Between Magnesium and Hydrochloric Acid.

The magnesium used in the experimental work was purchased from Magneson Elektron Ltd., and had a purity of 99.9%. In all of the reactions carried out the magnesium was in the form of cylinders. The diameter of the smallest cylinders was about 1 cm., while the largest cylinder used had a diameter of about 7.6 cm. Most cylinders had a lengths of about 4 cm., but a few of the larger ones were about 2 cm. long. Each 4 cm. long cylinder had a circular hole about 2 cm. deep and 0.5 cm. wide tapped at one end with a Whitworth 30 thread to receive the end of the stirring shaft, the end of which had been machined to produce the same thread. For the 2 cm. long cylinders the depth of the hole was about 1 cm.

Those parts of the cylinder surface which it was not desired to expose to attack by acids were protected by collodion flexile. A solution of collodion was carefully smeared on the magnesium surface to be protected and the cylinder, resting on a watch glass, was left to dry for 10-20 minutes in an electric oven. The cylinder was then taken out of the oven, allowed to cool in the air for a time, and then in a desiccator until it had reached room temperature. It was then weighed, replaced in the oven for a further 10 minutes or so, removed to cool as before, and reweighed. This procedure was repeated until the weight of the cylinder had attained a constant value.

For some experiments the surfaces to be exposed to attack by acid were polished beforehand with fine emery paper. In some cases the cylinder surfaces were treated with dilute acid solutions (acetic or hydrochloric acids) for a short while, washed with distilled water, and then the cylinders were dried to constant weight in an oven. For some

experiments, however, the magnesium surfaces to be exposed to acid attack received no prior treatment.

Two methods were used to follow the reactions between the magnesium and the acid solutions. These were (a) by weight-loss determinations, and (b) by noting the volume of hydrogen gas evolved. In the weight-loss method, it was simply necessary to weigh the magnesium cylinder before and after immersing it in the acid solution for a known period of time. The cylinder had of course to be thoroughly washed with distilled water after removal from the reaction vessel, then dried and cooled to room temperature before reweighing it. Using method (b), the volume of gas evolved in the reaction was read off at definite intervals by the use of a gas burette connected to the reaction vessel. It was necessary to determine both the atmospheric pressure and the temperature of the collected gas in order to calculate the volume of hydrogen that could theoretically be produced, under these conditions, if all the acid were used up.

Figure 2 shows the set-up of the apparatus for a gas-volume determination. The reaction vessel A was a 500 c.c. glass conical flask with a side tube E. A circular piece 7 cm. in diameter had been cut centrally from the base of this flask and slabs or membranes C of suitable material could then be placed across the circular opening and clamped in position by the special clamp B. This arrangement was to allow for experiments involving the use of ultrasonic waves. The gas produced during the reaction was led to a gas burette J surrounded by a water jacket K. This burette was graduated in divisions of 0.1 c.c., from 0 to 100 c.c. Water was pumped through K from the thermostat D, and the temperature of this water could be read on the thermometer L. G was a three-way tap in the connecting tube between J and A, the tube having an internal diameter of about 6 m.m. The stirrer shaft was driven by a motor H, the shaft being connected at M to the sheathed cable N from the motor by means

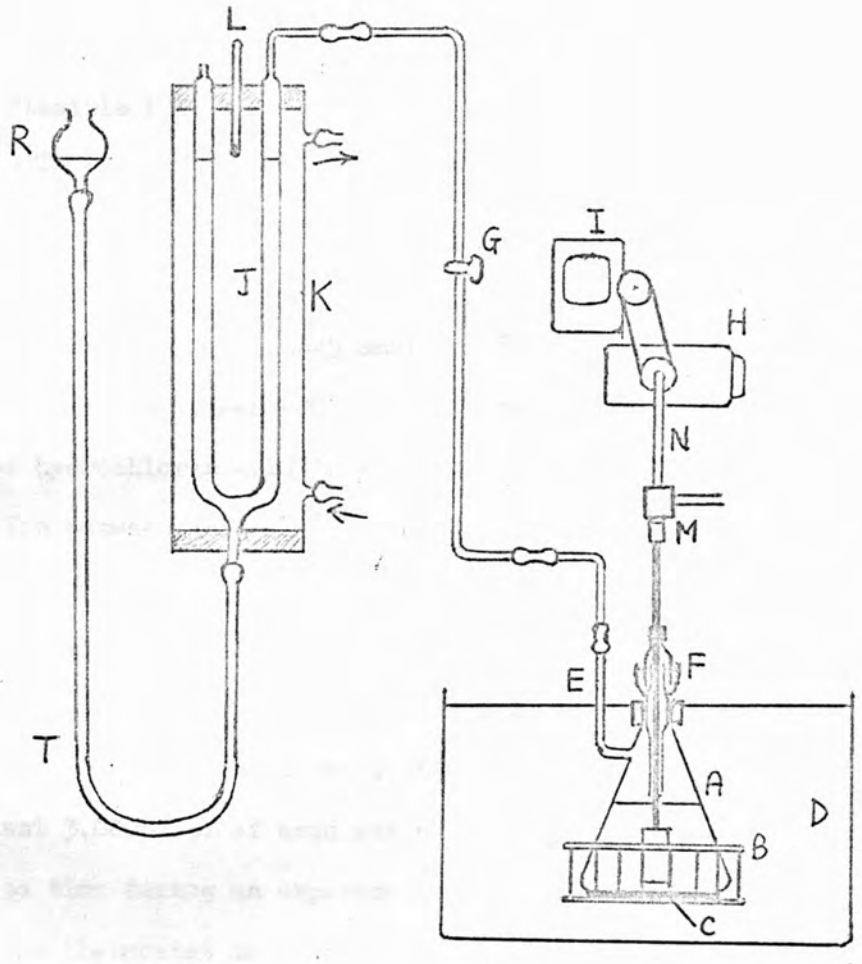


Figure 2

of a screw. The tachometer I, which registered the number of revolutions performed per minute by the cylinder, was connected to N by a pulley arrangement. F was an efficient mercury seal. The volume of gas collected was always measured at atmospheric pressure, and for levelling purposes the reservoir R could be moved up or down, being connected to the gas burette by a flexible rubber tube T.

In many of the weight-loss determinations the reaction vessels were open beakers suitably placed in the thermostat. A 5,000 c.c. glass beaker was used in some of the experiments that involved the use of 3,000 c.c. of acid solution, while a much smaller, 600 c.c. glass beaker was used when the volume of acid was 400 c.c. or less. Some experiments necessitated the use of hydrochloric acid in the concentration range of 1 to 3 N, and the reaction between acid of this concentration and the magnesium evolved considerable heat. Consequently in order to maintain conditions as near isothermal as possible, a large 10,000 c.c. cylindrical stainless steel bucket was used: the metal walls of the reaction vessel ensured a rapid flow of heat from the acid solution to the cooler water surrounding the steel bucket. At least 3,000 c.c. of acid was placed in this vessel at any one time. From time to time during an experiment with the steel vessel iced water was poured into the thermostat to minimise the rise in temperature due to the reaction between the magnesium and acid solution.

The ultrasonic generator used in this investigation was a type 125FF, purchased from Macrosonics Corporation, of New Jersey, U.S.A. It was worked off a one phase 120 volts A.C. supply at 60 cycles/sec., and had a maximum average acoustic power output of 25 watts. The nominal ultrasonic frequency of the generator was 800 kilocycles/sec. Ultrasonic waves were transmitted through a liquid medium as a result of the vibrations of the transducer disc of diameter 1.95 cm., housed in a cylindrical stainless steel unit, the dimensions of which are shown in Figure 3. This transducer unit was electrically connected to the generator through a long insulated flexible cable.

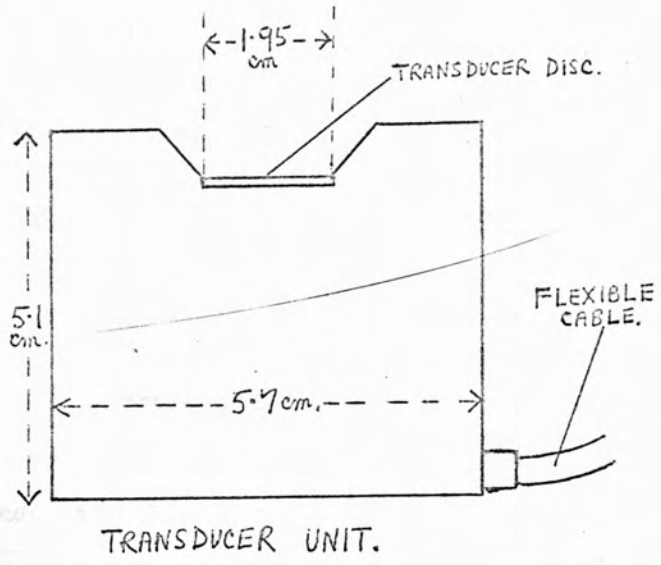

1·95 cm
TRANSDUCER DISC.
5·1 cm.
FLEXIBLE CABLE.
5·7 cm.
TRANSDUCER UNIT.

Figure 3

II(b) Methods of Expressing Results

It has been found by experiment[47] that, for a fixed volume of solution and constant apparent area of the solid surface, many heterogeneous reactions follow a first order rate law:

$$-\frac{dc}{dt} = k'[c] \qquad \ldots\ldots (1)$$

where c is the concentration in suitable units of the reacting solute and k' is the rate constant for a given volume and given apparent surface area. The value of k' varies from reaction to reaction and is also temperature dependent. Kilpatrick and Rushton[39] made a detailed experimental study of the effect of varying the volume of solution and the surface area of solid on the rate of the reaction between the curved surface of magnesium cylinders and dilute hydrochloric acid at 25°C. They found that the rate $(-\frac{dc}{dt})$ was directly proportional to the apparent surface area A and inversely proportional to the volume V of the hydrochloric acid solution. Therefore the rate equation can now be expressed as

$$-\frac{dc}{dt} = k\frac{A}{V}[c] \qquad \ldots\ldots (2),$$

where k' of equation (1) and k of equation (2) are related by the relationship $k' = k\frac{A}{V}$. The constant k is known as the rate constant per unit area at unit volume, or simply as the unit rate constant. In chemical engineering terminology it is frequently referred to as the coefficient of transport.

In order to obtain an integrated rate expression for first order heterogeneous reactions between solids and liquid reagents, it is necessary to integrate equation (2). This is easily done by the method of separation of variables. Choosing our limits of integration as the concentration c_o of solute at the commencement of reaction (t = o) and the concentration c_t

of solute at a time t after commencement of reaction, we have:

$$-\int_{c_o}^{c_t} \frac{dc}{c} = k\frac{A}{V}\int_{o}^{t} dt$$

i.e. $$-\left[\log c\right]_{c_o}^{c_t} = k\frac{A}{V} \cdot t,$$

or $$\log c_o/c_t = k\frac{A}{V} \cdot t \qquad \ldots\ldots (3)$$

For the experiments described here we have to relate the volume of hydrogen liberated, or the loss in weight of the cylinders, to the concentrations c_o and c_t in equation (3) in order to check the form of the rate equation and to calculate the rate constants. This can be done because c_o is directly proportional to H_o, the volume of hydrogen gas which would be produced under the conditions of the experiment if all the acid were used up, and c_t is directly proportional to $(H_o - H_t)$ where H_t is the volume of hydrogen liberated in time t after the commencement of the reaction. Deviations from the simple gas laws may be neglected at pressures near atmospheric and at a temperature of 25°C, so that direct proportionality between acid concentration and gas volume can be assumed. Therefore we can rewrite equation (3):

$$\log \frac{H_o}{H_o - H_t} = \frac{kA}{V} \cdot t \qquad \ldots\ldots (4)$$

In the case of a weight-loss determination, the initial concentration c_o of acid is directly proportional to the amount a of magnesium which would dissolve if all the acid were used up. (C.V.King calls this the solution capacity of the acid) while c_t is directly proportional to a-x, where x is the amount of magnesium that has dissolved

in a time t from the commencement of the reaction. Therefore we have:

$$\log \frac{a}{a - x} = \frac{kA}{V} \cdot t \qquad \ldots\ldots \quad (5)$$

When a series of volume measurements is available for a given kinetic run, we can test the reaction for first order kinetics by rearranging equation (4) to give $\log_{10}(H_o - H_t) = \log_{10} H_o - \frac{kA}{2.303V} \cdot t$, and hence plotting $\log_{10}(H_o - H_t)$ values as ordinates against values of t as abscissae. If the reaction is of the first order, the points should lie on a straight line with a negative slope equal to $\frac{kA}{2.303V}$ and an intercept on the y-axis equal to $\log_{10} H_o$. If the numerical value of the slope is m, then

$$k = \frac{2.303Vm}{A} \qquad \ldots\ldots \quad (6),$$

an equation that enables us to calculate the unit rate constant. A similar treatment to that applied to equation (4) can be applied to equation (5).

II(c) Experiment to Determine the Order of the Reaction between Magnesium and Dilute Hydrochloric Acid at 25.4°C.

The experimental set-up of Figure 1 was used for the experiment. Kilpatrick and Rushton[39] have shown that no gas other than hydrogen is produced in the reaction between dilute hydrochloric acid and magnesium. 300 c.c. Of 0.03345 N HCl were pipetted into the conical reaction vessel, which had been thoroughly cleaned and dried beforehand. A magnesium cylinder of length 3.95 cm. and mean diameter of 1.981 cm. was used. Measurements of the diameter were taken at six places, two near each end of the cylinder, and two near its middle, by means of a micrometer gauge. The cylinder, revolving at a speed of 200 revolutions per minute, was quickly lowered into the acid and a stop clock simultaneously started. Readings of volume on the gas burette were taken at one minute intervals for 15 minutes. Care was continually taken to ensure that the cylinder rotated at 200 r.p.m. by controlling the electric motor. At the end of this time the cylinder was quickly removed from the reaction vessel, washed with distilled water, then dried in readiness for a further experiment. The pressure of the atmosphere was recorded.

Values of time and volume of hydrogen collected are recorded in Table 1. It will be noticed that the volume at zero time is not 0 but 1.2 c.c. Although the levels of the distilled water in the gas burette were opposite the zero volume mark before the cylinder was lowered into the acid, there was a certain compression effect when the cylinder was quickly lowered into position, with the consequence that the level of water in the right hand limb of the burette (c.f. Figure 2) was somewhat depressed. A preliminary test, with 300 c.c. of water instead of acid in the reaction flask and a cylinder of the same dimensions as the one used

in the experiment, showed that the water menisci, upon adjustment of the height of the reservoir R, became level again opposite the 1.2 c.c. mark on the burette. Therefore the zero-time volume was 1.2 c.c.

Table 1

Time in minutes	Volume in c.c.
0	1.2
1	5.9
2	11.0
3	15.2
4	20.0
5	23.9
6	27.8
7	31.4
8	34.9
9	38.2
10	41.5
11	44.6
12	47.7
13	50.6
14	53.4
15	56.1

Details of the calculation of the volume of hydrogen H_o that would be produced if all the acid were used up are as follows:

Exhaustion of 300 c.c. of 0.03345 M HCl would yield $(0.3 \times 0.03345 \times 22{,}414)/2$ c.c. of H_2 at S.T.P.

In the experiment described T = 298.6° Abs. and the atmospheric pressure was 770.0 m.m. of mercury. The pressure due to the hydrogen gas is the measured atmospheric pressure less the pressure of the saturated water vapour in the enclosed space. The pressure of saturated water vapour at 25.4°C is 24.3 m.m. of mercury, so the actual pressure of the hydrogen = 745.7 m.m. Multiplying the S.T.P. volume appropriately we deduce that the apparent value of H_o is 125.3 c.c.

As the volume increments during the first few minutes of these reactions do not decrease steadily, it was decided to take, in this case, as our starting point for the purpose of calculating H_t the volume at four minutes. Therefore H_o = 125.3 - (20.0 - 1.2) = 106.5 c.c. Table 2 gives the values of $\log_{10}(H_o-H_t)$ which are needed to test for first order kinetics.

Table 2

H_t (c.c.)	H_o-H_t	$\log_{10}(H_o-H_t)$	t (minutes)
3.9	102.6	2.0111	1
7.8	98.7	1.9943	2
11.4	95.1	1.9782	3
14.9	91.6	1.9619	4
18.2	88.3	1.9460	5
21.5	85.0	1.9294	6
24.6	81.9	1.9133	7
27.7	78.8	1.8965	8
30.6	75.9	1.8802	9
33.4	73.1	1.8639	10
36.1	70.4	1.8476	11

Figure 4

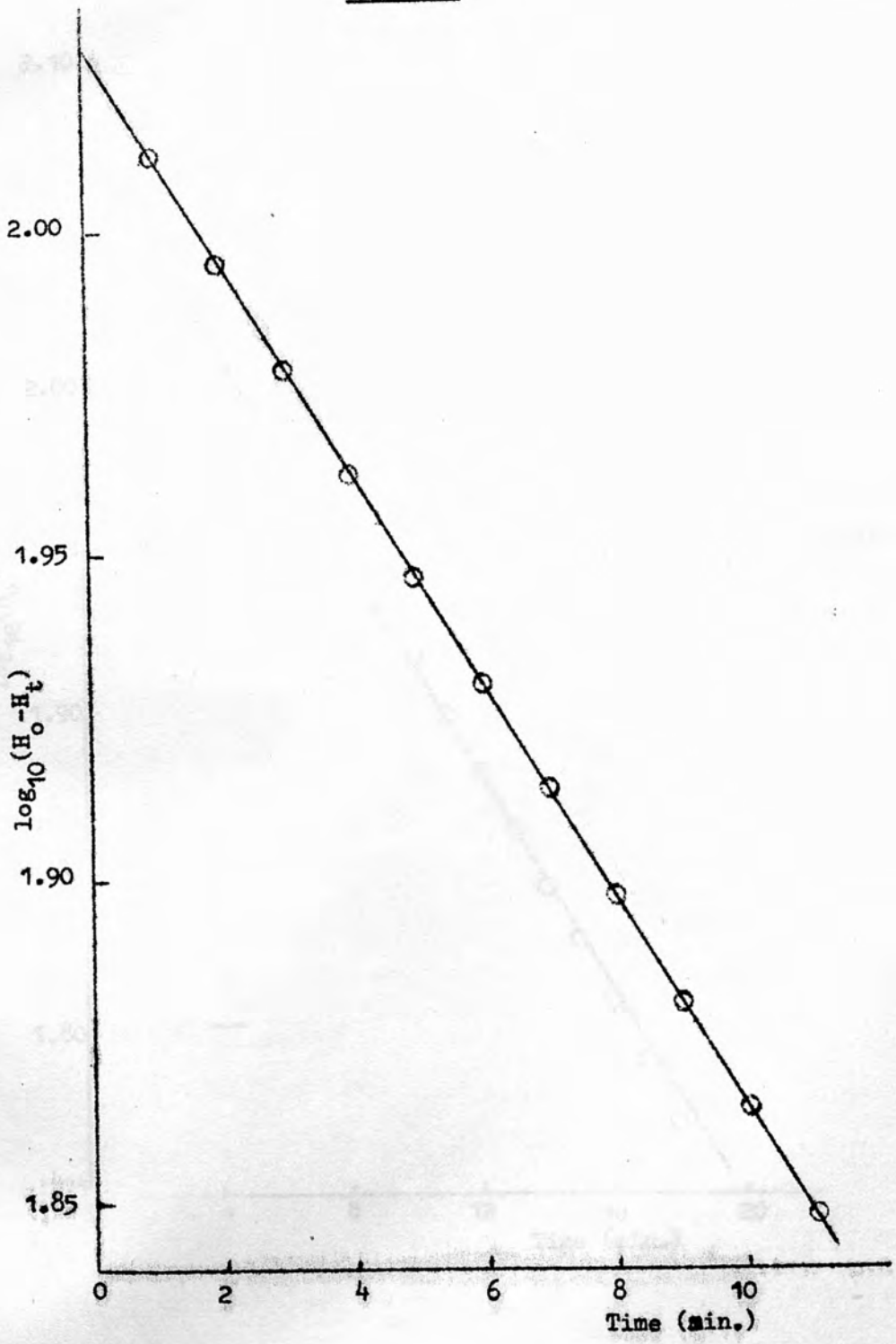
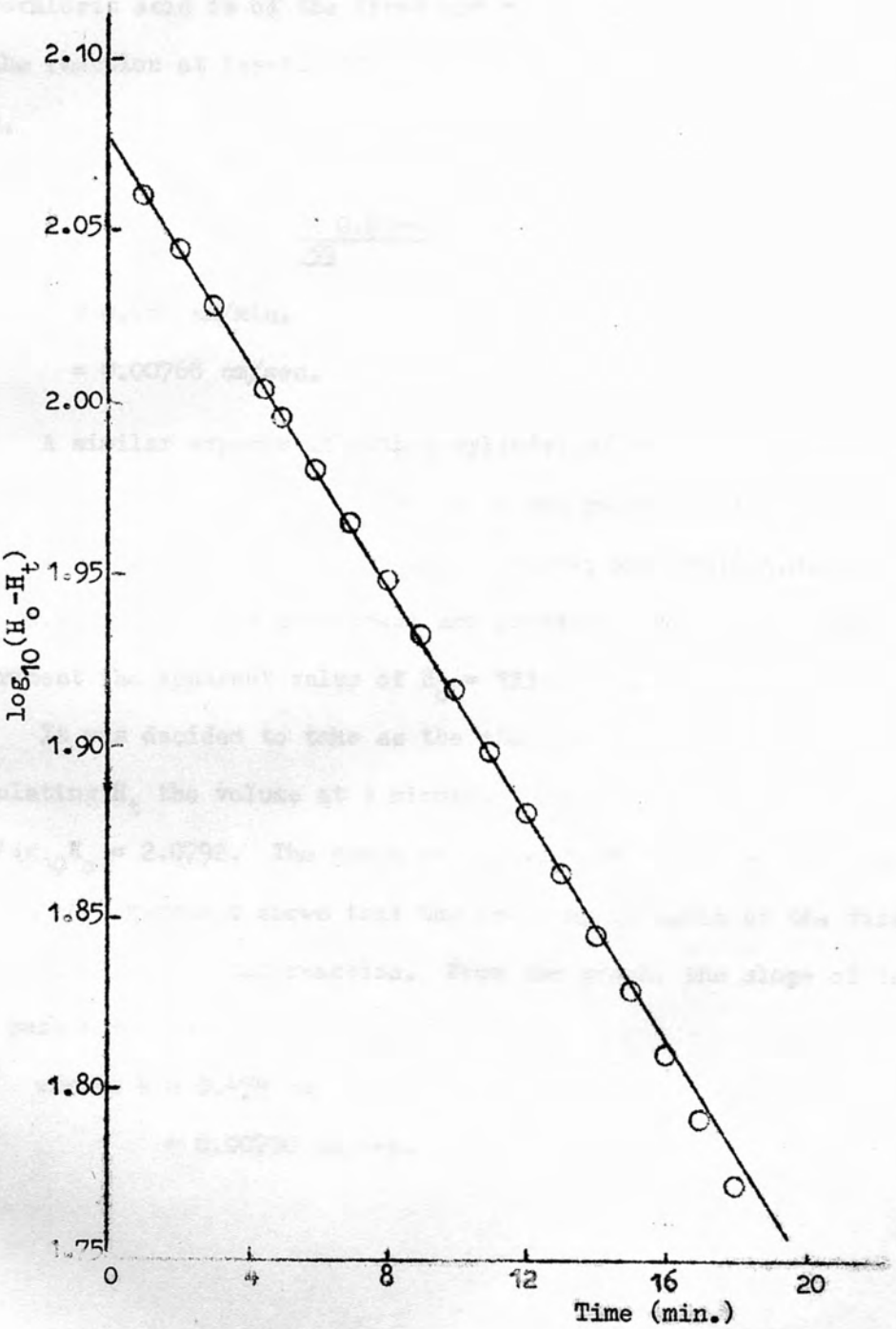


Figure 5



The values of $\log_{10}(H_o - H_t)$ as ordinates are plotted against the corresponding values of t as abscissae in Figure 4. The straight line graph obtained shows that the reaction between magnesium and 0.03345 M hydrochloric acid is of the first order in acid concentration, over 40% of the reaction at least. If we denote the numerical value of the slope by m,

m = 0.0164, and from equation (6), Section II(b)

$$k = \frac{2.303 \times 300 \times 0.0164}{24.59}$$

= 0.461 cm/min.

= 0.00768 cm/sec.

A similar experiment with a cylinder of mean diameter 1.926 cm. in 300 c.c. of 0.03295 M hydrochloric acid was performed at 25.4°C and a speed of 200 r.p.m. The pressure of the atmosphere was 768.6 m.m. of mercury. The data collected in this experiment are presented in Tables 3 and 4. For this experiment the apparent value of H_o = 123.7 c.c.

It was decided to take as the starting point for the purpose of calculating H_t the volume at 1 minute. Therefore H_o = 123.7 - 3.7 = 120.0 c.c. and $\log_{10}H_o$ = 2.0792. The graph of Figure 5 obtained by plotting $\log_{10}(H_o - H_t)$ versus t shows that the reaction is again of the first order over about 40% of total reaction. From the graph, the slope of the straight line part = - 0.0164,

whence k = 0.474 cm/min.

= 0.00790 cm/sec.

Table 3

Time in minutes	Volume in c.c.
0	1.2
1	4.9
2	9.9
3	14.0
4	18.0
5.1/2	23.9
6	25.8
7	29.2
8	32.6
9	36.0
10	39.2
11	42.4
12	45.7
13	48.9
14	51.8
15	54.8
16	57.4
17	60.2
18	63.0
19	65.6
20	68.2

Table 4

H_t (c.c.)	$H_o - H_t$	$\log_{10}(H_o - H_t)$	t (minutes)
5.0	115.0	2.0603	1
9.1	110.9	2.0445	2
13.1	106.9	2.0286	3
19.0	101.0	2.0039	4.5
20.9	99.1	1.9956	5
24.3	95.7	1.9805	6
27.7	92.3	1.9647	7
31.1	88.9	1.9484	8
34.3	85.7	1.9325	9
37.5	82.5	1.9159	10
40.8	79.2	1.8982	11
44.0	76.0	1.8802	12
46.9	73.1	1.8633	13
49.9	70.1	1.8451	14
52.5	67.5	1.8287	15
55.3	64.7	1.8102	16
58.1	61.9	1.7910	17
60.7	59.3	1.7723	18
63.3	56.7	1.7528	19

The agreement between the rate constants for these two experiments seems satisfactory (within 2.1/2%). The slight differences between the diameters of the two cylinders and the concentrations of the hydrochloric acid solutions used in the experiments are considered not to affect the values of the constants to any significant extent.

II(d) Correlation of the Methods of Analysis

Calculations of rate constants have sometimes been based upon measurements of volume of hydrogen evolved and in other cases on measurements of weight of magnesium dissolved. It is desirable to show whether or not these two kinds of observation lead to similar quantitative conclusions.

For this purpose the apparatus shown in Fig. 2 was used. In each experiment a magnesium cylinder was rotated in a solution of a certain acid of known concentration. At a definite time the volume of hydrogen evolved was noted, and the cylinder was immediately removed from the acid, washed with distilled water and dried to constant weight. Table 5 records the results of a selection of such experiments, using (A) acetic acid; (B) formic acid; (C) hydrochloric acid.

Table 5

Acid/Conc. (M)	Weight loss (g)	Vol.(H_2) (c.c)	T°C	Press. (m.m.)	Moles H_2 evolved x 10^3	Moles Mg dissolved x 10^3
A. 0.105	0.0794	77.0	25.0	761.85	3.06	3.26
0.105	0.0894	92.8	25.0	758.3	3.67	3.68
0.105	0.0960	97.4	25.0	758.8	3.85	3.95
0.026	0.0702	74.9	25.0	757.8	2.96	2.89
0.026	0.0585	61.1	25.0	758.8	2.42	2.41
0.026	0.0465	49.6	25.0	761.0	1.97	1.91
0.026	0.0640	66.9	25.0	760.0	2.65	2.63
0.026	0.0851	85.8	25.0	760.0	3.40	3.50
B. 0.025	0.0543	59.9	25.0	752.65	2.35	2.23
0.025	0.0658	68.5	25.0	751.0	2.68	2.71
0.025	0.0656	67.3	25.0	749.6	2.63	2.70
C. 0.0659	0.0064	6.3	25.5	763.0	0.25	0.26
0.0659	0.0070	7.2	25.5	763.0	0.29	0.29
0.0659	0.0066	6.2	25.5	764.0	0.25	0.27

The mean value of the ratio of the figures in Col. 7 to those in Col. 6 is 1.00 (8). This agreement is satisfactory, and the array of results also gives some indication of the reliability of rate constants based upon a single observation.

Further demonstration that the two experimental methods measure the same quantity is obtained by comparing rate constants obtained by the two methods from completely separate experiments performed under the same conditions. Two series of runs (carried out eight months apart) were made in which only the lower ends of magnesium cylinders of diameter 2.00 cm were exposed when rotated at 200 r.p.m. in 300 c.c. of 0.0659 M hydrochloric acid at 25.5°C. Five runs made observing volume measurements gave an average rate constant of 0.66 cm/min; whereas (cf. Table 30) the mean value of k from nine experiments based on weight losses was 0.69 cm/min.

It was also felt necessary to compare weight losses from magnesium cylinders with the corresponding changes in the dimensions of the cylinders. Firstly this checks whether the collodion-covered parts of the rotor are immune from attack, and secondly it enables one to investigate whether cylinders retain their general right-cylindrical shape and hence whether the true surface areas remain, approximately at least, the apparent geometrical areas.

Concerning the first objective, several scattered experiments were performed in which cylinders of length 3.95 cm. were rotated in hydrochloric acid under a variety of conditions of angular velocity, acid concentration, temperature, and cylinder radius. Losses in weight, and initial and final dimensions of the cylinders were measured. These cylinders all had only the curved surface exposed, and in each case six standardised caliper measurements were made of the diameters before and after the experiment.

The observations are collected in Table 6. The correlation between Cols. 6 and 7 shows that attack did not take place on the flat protected surfaces.

Concerning the second point mentioned above, in a typical experiment involving a large weight loss (3.7463 g) the six measured diameters altered from an initial 1.934 $\pm$ 0.011 cm to a final value of 1.751 $\pm$ 0.014 cm. Attack was thus uniform along the cylinder and there was no significant deviation from a right-cylindrical shape during reaction.

Table 6

Conc.HCl (M)	T°C	r.p.m.	Mean d_i (cm)	Mean d_f (cm)	Weight loss (g) calc.	Weight loss (g) obs.
1.166	25.5	1000	2.001	1.874	2.68	2.6647
1.166	25.5	1000	1.874	1.793	1.62	1.6722
1.166	25.5	1000	1.793	1.713	1.53	1.4899
1.166	25.5	1000	1.713	1.643	1.28	1.2924
1.166	25.5	1000	1.643	1.578	1.14	1.1389
1.166	25.5	1000	1.578	1.516	1.04	1.0009
1.450	4.0	4000	2.000	1.923	1.64	1.6524
2.852	25.5	1000	1.914	1.760	3.08	3.3518
2.852	15.0	1000	1.923	1.760	3.26	3.3692
2.852	14.0	4000	1.931	1.753	3.57	3.7463

II(e) Experiments to Determine the Temperature Coefficient of Reaction between Dilute Dydrochloric Acid and Magnesium.

A series of seven experiments was carried out, three of them at a temperature of 25.4°C, a pair at 35.4°C and a pair at 44.2°C. The experimental set-up of Figure 2 was used, the volume of dilute hydrochloric acid in the reaction flask being 300 c.c. in every experiment. There was a slight variation in the initial diameters of the cylinders in this series of experiments, amounting to about 2.1/2% between the smallest and largest diameters (see Table 8). Also it will be noticed in the same table that the concentration of the acid in the first three experiments was about 1.1/2% higher than the concentration of the acid in the last four experiments. In each experiment the cylinder was rotated at 320 rp.m.

The volumes of hydrogen gas collected at the corresponding times from the start of the experiment are recorded in Table 7, which also shows the temperature of the reaction and the atmospheric pressure in each experiment. As previously explained, the reading on the gas burette at zero time was 1.2 c.c. The same method of expressing the results as was used in the previous section was adopted with the data of these seven experiments, and the $\log_{10}(H_o - H_t)$ versus t plots are shown in Figures 6 to 12. Each one of the seven graphs shows an initial straight part followed by a downward curve, which shows that the reaction in the later stages is proceeding faster than expected from the slope of the initial straight part. The straight line drawn in each figure passes through the theoretical first order intercept, $\log_{10}H_o$, for a first order reaction. The first order rate constants k are calculated from the slopes of these straight lines, and the $\bar{k}$ values are recorded in Table 8. In the third column of Table 9 are recorded the average values of the rate constants at each of the three temperatures.

The values of the temperature coefficient of the magnesium/dilute hydrochloric acid reaction were calculated from the data of Table 7, thus

$$\frac{k^*_{35.4}}{k^*_{25.4}} = \frac{0.0133}{0.0107} = 1.24,$$

and $$\frac{k^*_{44.2}}{k^*_{35.4}} = \frac{0.0160}{0.0133} = 1.20$$

The data of Table 9 were also used to produce an Arrhenius plot, values of $2 + \log_{10}k^*$ being plotted against the corresponding values of $^1/_T$. The result is shown in Figure 13. From the Arrhenius equation,

$$k^* = A\, e^{-E/RT},$$

we have upon taking logarithms:

$$\log_{10}k^* = \log_{10}A - \frac{E}{2.303RT}.$$

Numerically the slope m of the straight line obtained by plotting $\log_{10}k^*$ versus $^1/_T$ is equal to $^E/_{2.303R}$. From Figure 13, m = - 911 whence E = 4.1 (7) kilocalories per mole.

It will be noticed that the value of the temperature coefficient and hence of the activation energy for the reaction between magnesium and the dilute hydrochloric acid just calculated are typical of the values to be expected (from 3 to 6 kilocalories per mole) for a diffusion-controlled heterogeneous reaction between a solid and a liquid reagent.

Table 7

Time in minutes	Volume in c.c.						
	Experiment 1 Temp: 25.4 Press:750 mm	Experiment 2 Temp : 25.4 Press:758 mm	Experiment 3 Temp: 25.4 Press:758 mm	Experiment 4 Temp: 35.4 Press:764.3mm	Experiment 5 Temp: 35.4 Press:765 mm	Experiment 6 Temp: 44.2 Press: 755 mm	Experiment 7 Temp: 44.2 Press:754.5mm
1	4.8	4.5	4.8	5.3	5.8	8.2	10.3
2	11.3	11.3	11.2	13.2	13.3	17.9	21.2
3	17.1	17.7	17.4	20.7	20.5	27.0	29.7
4	22.0	23.4	23.4	27.7	27.3	35.6	37.9
5	27.0	28.8	28.8	34.2	33.8	43.6	45.6
6	31.7	34.0	33.9	40.3	39.7	51.0	53.0
7	36.4	38.9	38.5	46.4	45.5	57.9	59.9
8	41.0	43.5	43.1	52.0	51.1	64.4	66.3
9	45.5	47.8	48.0	57.2	56.4	70.3	72.4
10	50.4	52.1	52.3	62.0	61.4	76.0	78.0
11	56.2*	56.5	56.3	67.1	66.1	81.4	83.3
12	58.1	60.5	60.7	71.7	70.5	86.2	88.0
13	61.7	64.2	64.5	76.1	74.7	90.7	92.6
14	65.4	67.7	68.2	80.1	78.7	94.4	96.7
15	68.8	71.1	71.5				
16	72.1	74.2	75.3				
17	75.5	77.4	78.2				
18	79.1	80.3	81.4				
19	82.0	83.0	84.0				
20	84.6	85.5	86.5				

*read at 11.5 min.

Table 8

Experiment Number	Mean Cylinder Diameter (cm.)	Concentration of Acid (Molar)	H_o (cc.)	k (cm/sec)
1	1.988	0.0334(5)	125.1	0.0102
2	1.955	0.0334(5)	124.0	0.0109
3	1.960	0.0334(5)	123.7	0.0110
4	1.950	0.0329(5)	127.9	0.0135
5	1.943	0.0329(5)	127.2	0.0131
6	1.938	0.0329(5)	135.7	0.0158
7	1.935	0.0329(5)	133.7	0.0162

Table 9

Temperature T^oK	$1/T$	Mean Rate Constant k^*, (cm/sec.)	$2 + \log_{10} k^*$
298.6	0.003349	0.0107	0.0286
308.6	0.003240	0.0133	0.1232
317.4	0.003151	0.0160	0.2041

Figure 6

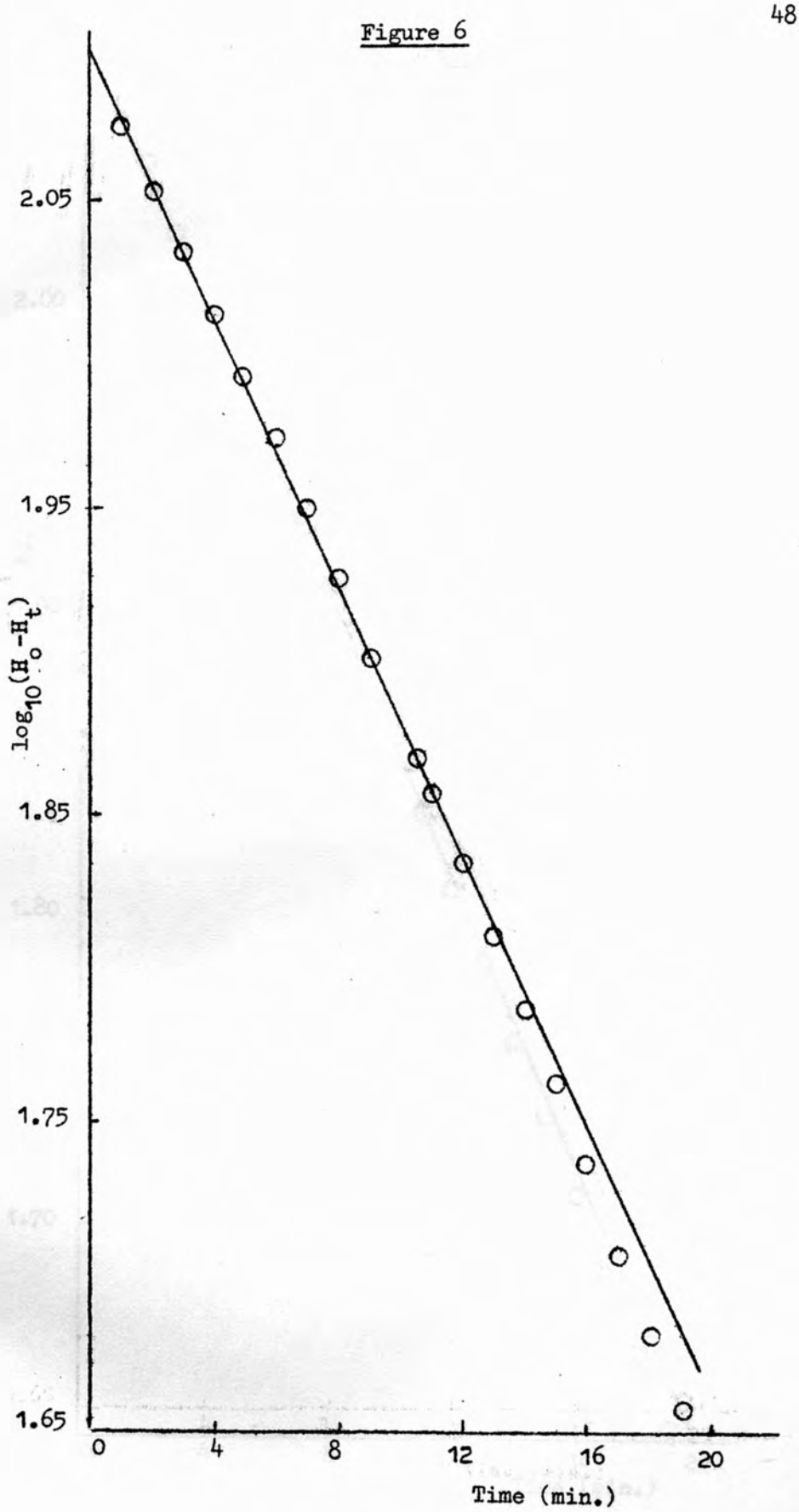


Figure 7

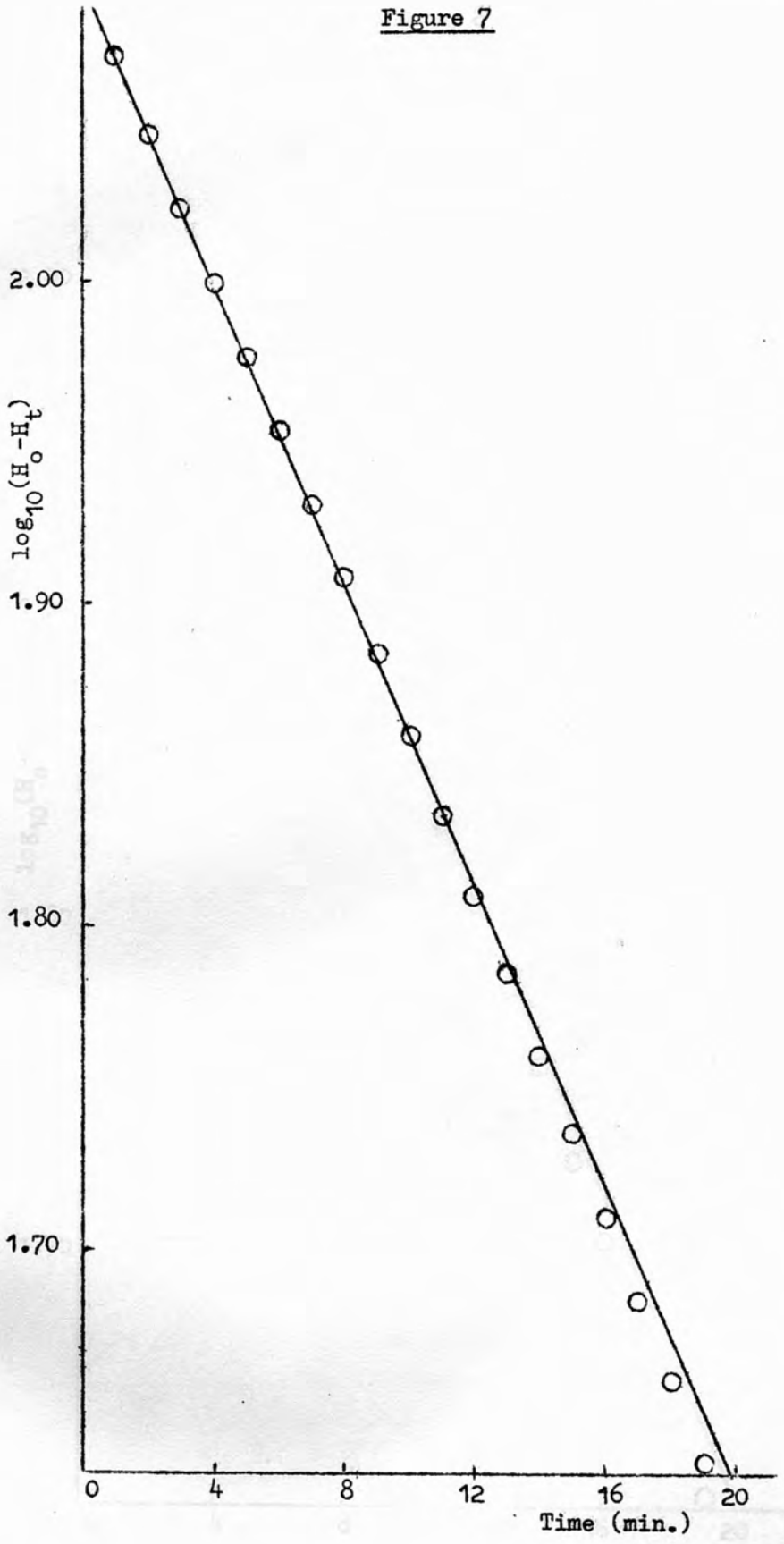


Figure 8

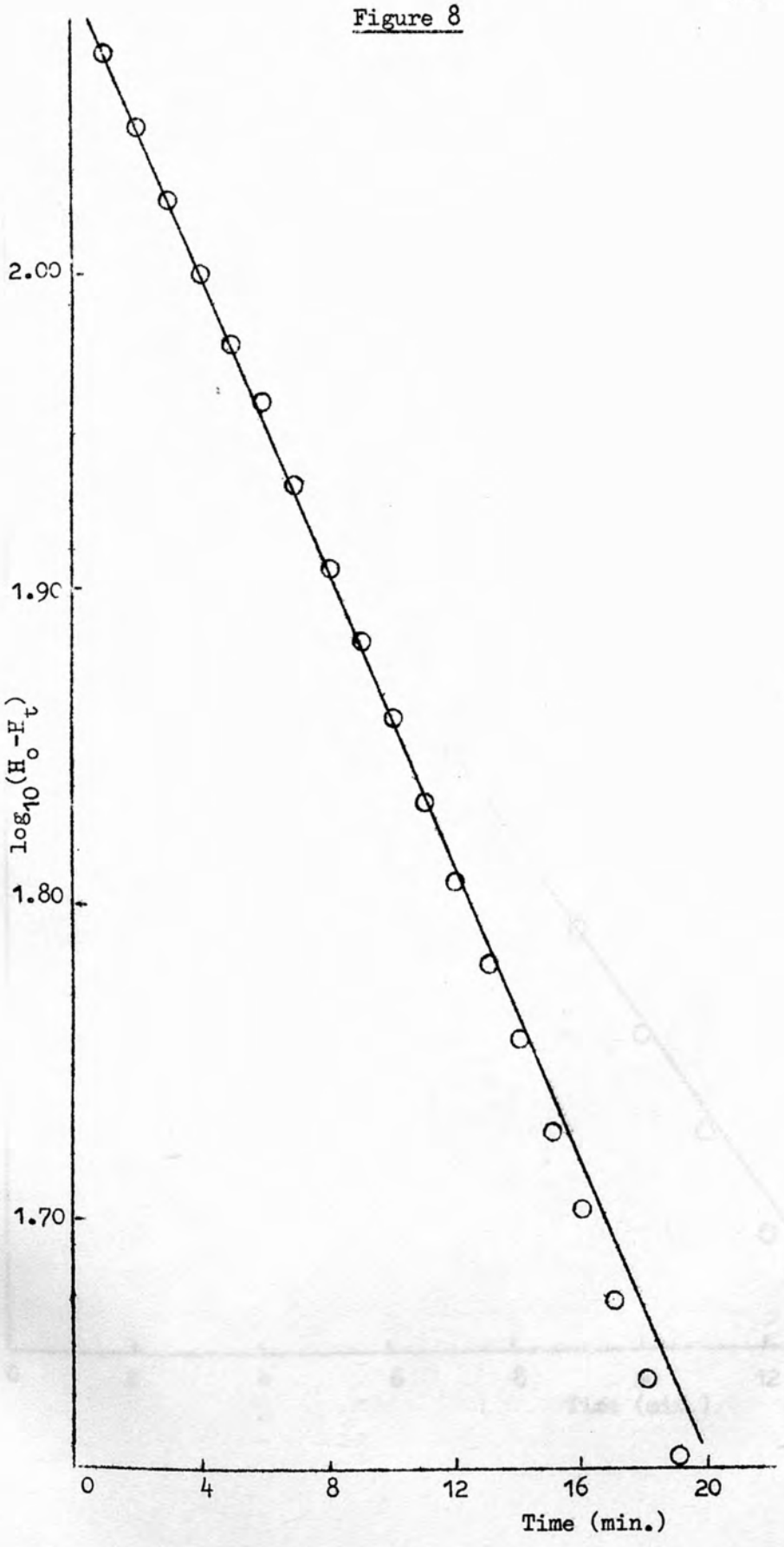


Figure 9

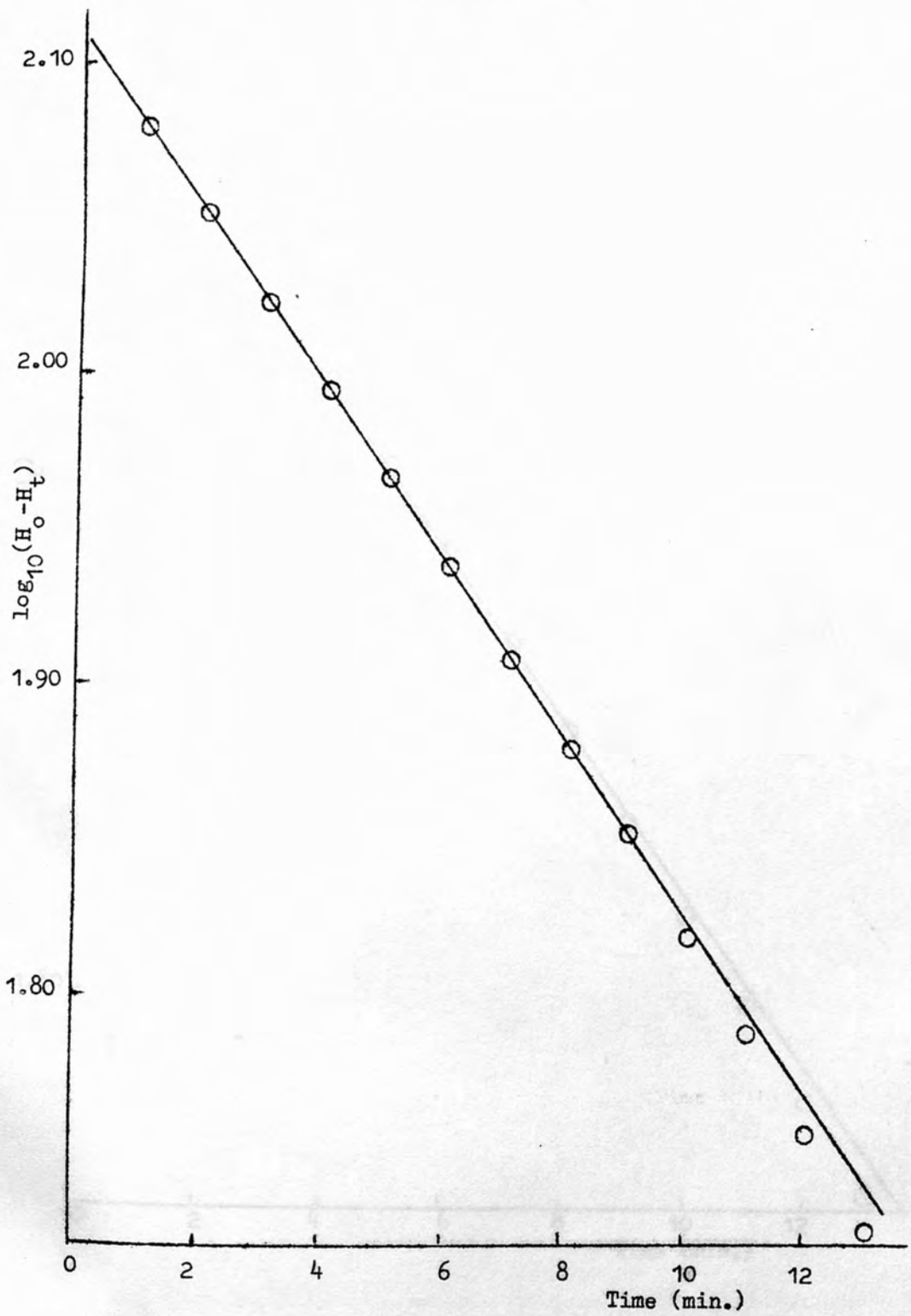


Figure 10

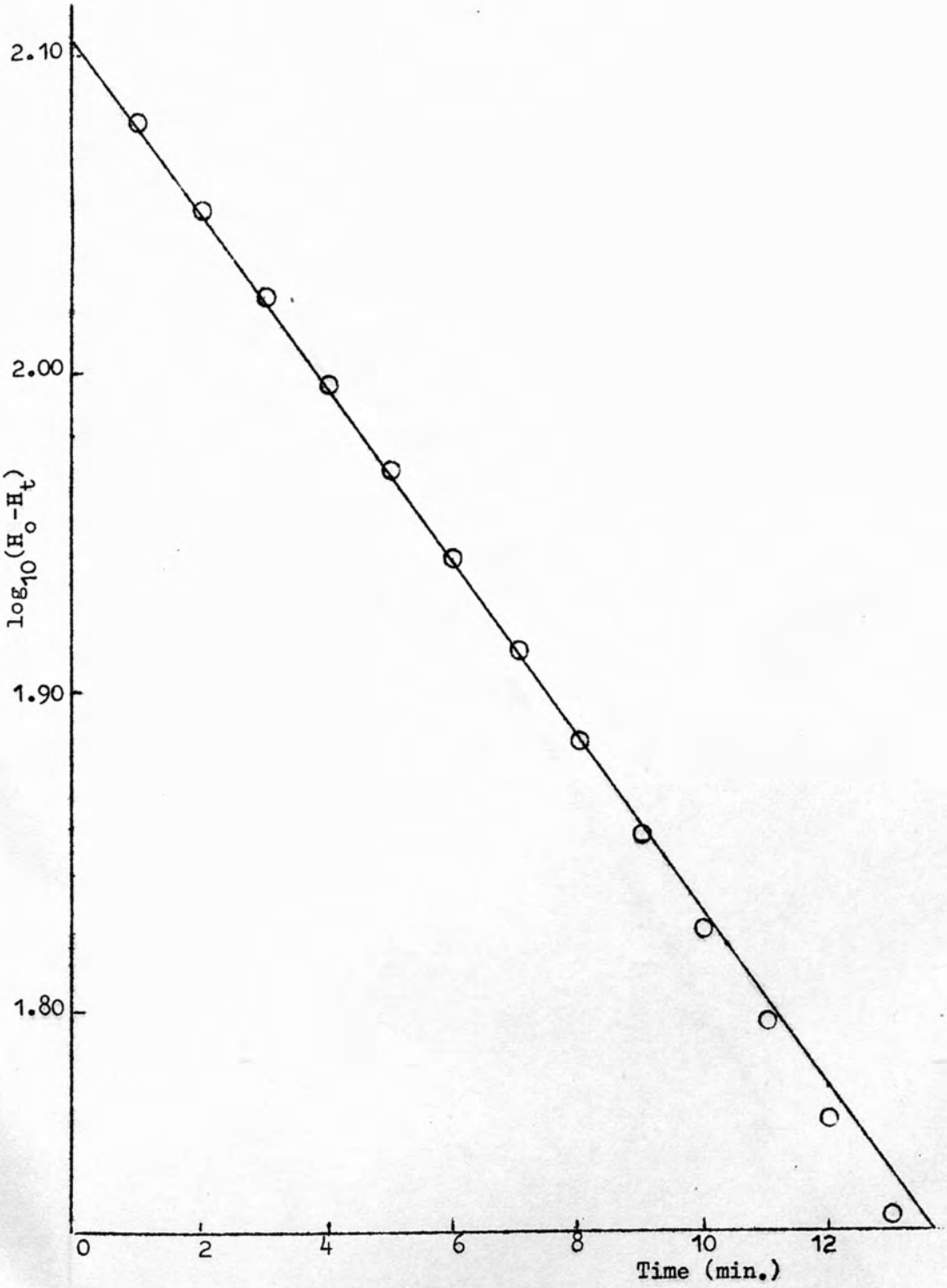


Figure 11

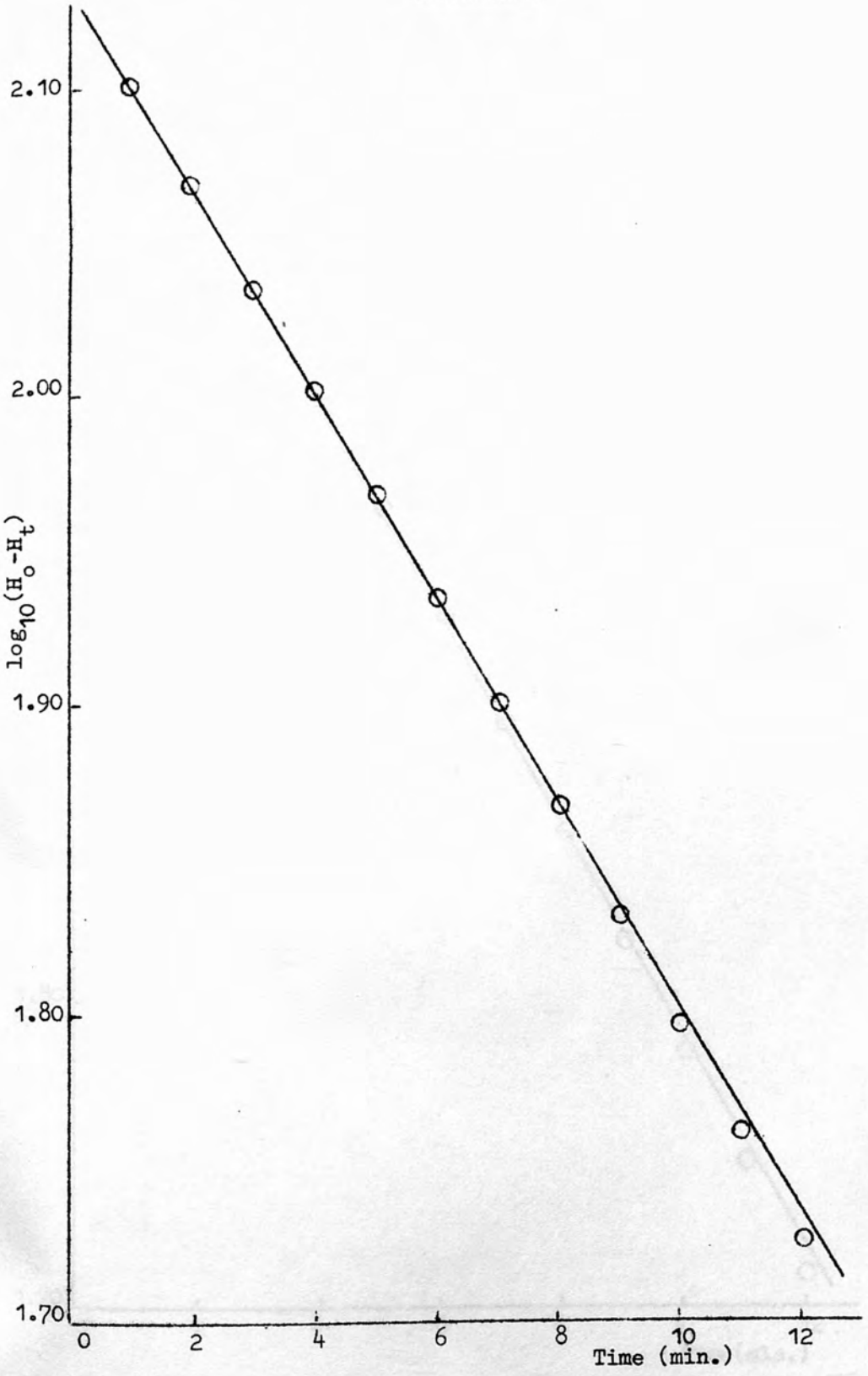


Figure 12

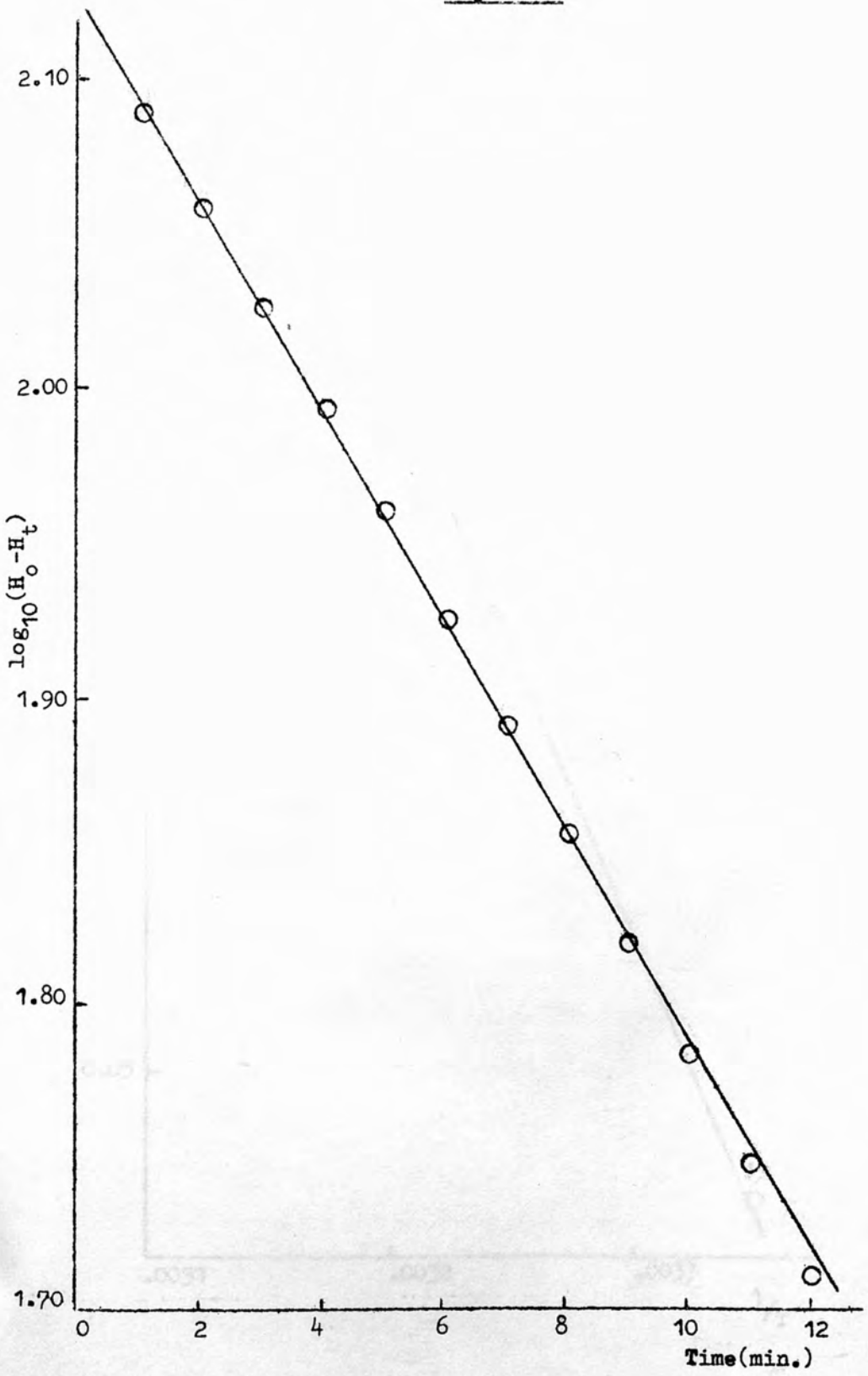
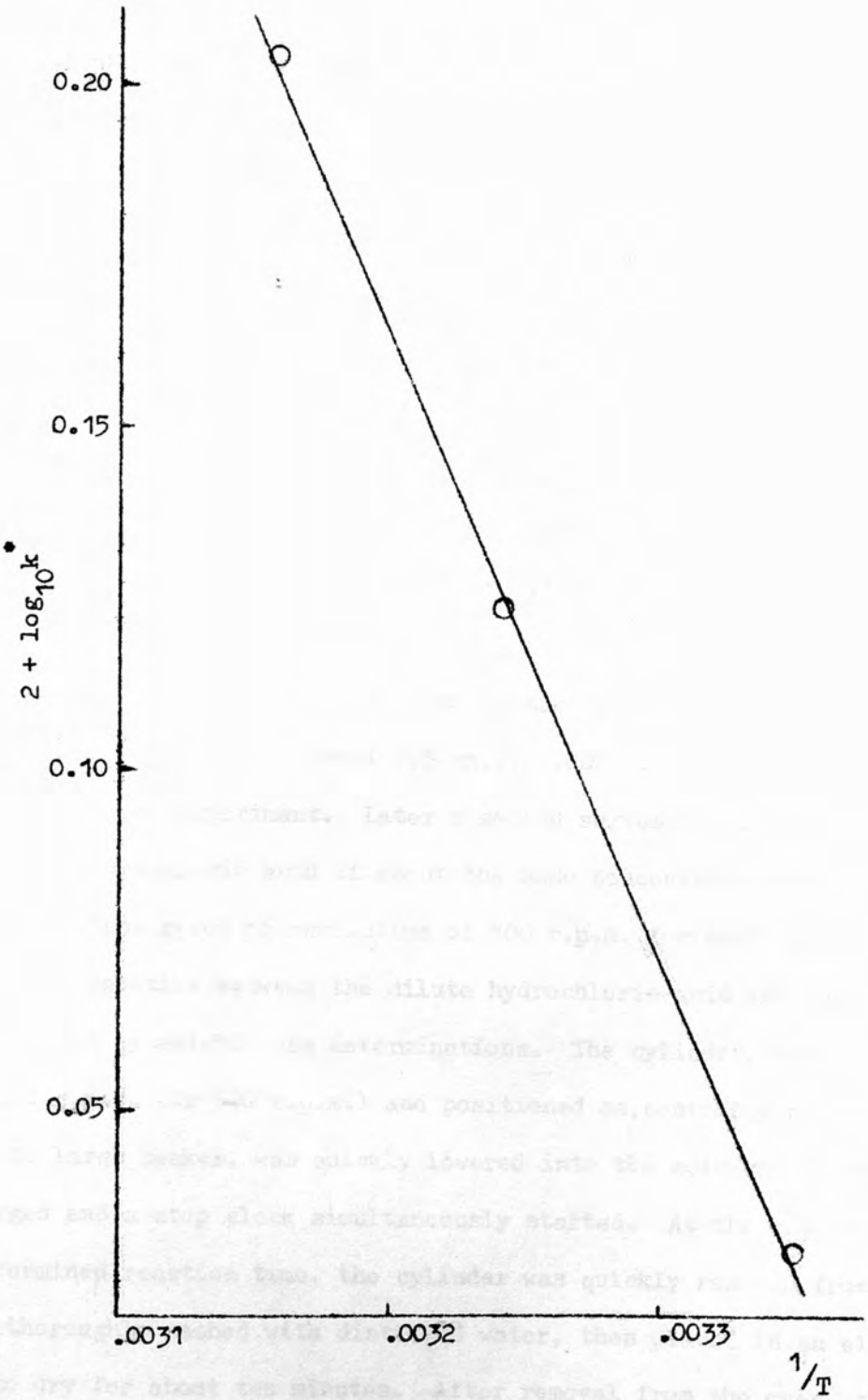


Figure 13



II(f) The Dependence of the Unit Rate Constant of a Heterogeneous Reaction on the Diameter of the Solid Cylindrical Specimen

As mentioned[32] in Section III(d), the work of Eisenberg, Tobias and Wilke has shown that the unit rate constant of a heterogeneous reaction between a liquid and the curved surface of a solid cylinder of diameter d may be proportional to $d^{0.4}$, provided data are obtained within the Reynold's Number range of 1,000 - 100,000. In order to test this relationship, a series of experiments was carried out involving the use of a number of magnesium cylinders of varying diameters but all of the same length, 3.95 cm. These experiments were conducted at a temperature of 25°C with dilute hydrochloric acid (about 0.06 N) and a constant speed of revolution of 1,000 r.p.m. for each cylinder. There is reason to believe that with acid of this concentration the reaction with magnesium at 25°C is virtually diffusion controlled, as were the reactions and processes studied by Eisenberg, Tobias and Wilke. As some of the cylinders were large (the largest had a diameter of about 7.5 cm.), 3,000 or 4,000 c.c. of acid was used in each experiment. Later a second series of experiments was done with hydrochloric acid of about the same concentration at 25°C, but with a constant speed of revolution of 500 r.p.m. for each cylinder.

The reaction between the dilute hydrochloric acid and magnesium was followed by weight loss determinations. The cylinder, revolving at 1,000 r.p.m. (or 500 r.p.m.) and positioned as centrally as possible over the large beaker, was quickly lowered into the acid until completely submerged and a stop clock simultaneously started. At the end of the predetermined reaction time, the cylinder was quickly removed from the acid, thoroughly washed with distilled water, then placed in an electric oven to dry for about ten minutes. After removal from the oven, the

cylinder was allowed to cool in the air for some time, and then inside a desiccator until it had reached room temperature. It was weighed, replaced in the oven for a further ten minutes or so, and, after cooling to room temperature, reweighed. This procedure was repeated until the cylinder had attained a constant weight.

Evidence exists, e.g. in the work of Kilpatrick and Rushton, that the reaction between magnesium and hydrochloric acid of concentration in the region of 0.06 N is of the first order with respect to acid concentration. Therefore the unit rate constants for the reactions in the work described above were calculated from the integrated expression for a first order reaction,

$$k = \frac{2.303V}{At} \log_{10}\left(\frac{a}{a - x}\right),$$

where the symbols have the meanings used earlier. The Reynold's Number for each experiment was calculated from the formula

$$R_d = \frac{Pd_i}{\nu} = \frac{\pi S d_i^2}{\nu}$$

where S = the number of revolutions performed per second by the cylinder, d_i = the diameter in cm. of the cylinder, and ν = the kinematic viscosity of the solution in cm^2/sec. Table 10 gives the data necessary for a statistical evaluation of the results. The figures in the seventh column show that the Reynold's Numbers for the experiments involving cylinders of diameters from 0.9854 cm. to 3.997 cm., are within the range 1,000 to 100,000, the range for which Eisenberg, Tobias and Wilke discovered their $k \propto d_i^{0.4}$ relationship. Consequently the results of these seventeen experiments were used in the following least squares treatment.

Table 10

d_i in cm.	Apparent area A of curved surface in sq. cm.	Loss in weight in grams (x)	Solution capacity in grams(a)	Reaction time in seconds	Unit rate constant k in cm/sec.	R_d	$2 + \log_{10} d_i$	$2 + \log_{10} k$
0.9854	12.23	0.0481	2.393	300	0.01675	5,645	1.9936	0.2240
0.9920	12.31	0.0494	2.391	300	0.01683	5,721	1.9965	0.2261
0.9925	12.32	0.044	2.367	300	0.01514	5,726	1.9967	0.1801
1.2256	15.22	0.062	2.400	300	0.01710	8,740	2.0885	0.2330
1.511	18.76	0.087	2.393	300	0.01989	13,280	2.1793	0.2987
1.707	21.18	0.099	2.393	300	0.02001	16,940	2.2322	0.3012
1.849	22.95	0.121	2.393	300	0.02268	19,870	2.2669	0.3556
1.855	23.02	0.1206	2.391	300	0.02240	20,000	2.2683	0.3502
1.975	24.51	0.123	2.393	300	0.02160	22,690	2.2956	0.3345
1.989	24.68	0.103	2.369	240	0.02250	23,000	2.2987	0.3522
1.9955	24.77	0.118	2.391	300	0.02036	23,150	2.3001	0.3088
2.500	31.02	0.141	2.366	240	0.02468	36,330	2.3979	0.3923
2.514	31.20	0.177	2.400	300	0.02450	36,750	2.4004	0.3892
2.996	37.19	0.176	2.354	240	0.02607	52,200	2.4766	0.4161
3.497	43.40	0.166	2.369	180	0.02795	71,100	2.5437	0.4464
3.989	49.51	0.207	2.367	180	0.03078	92,550	2.6009	0.4953
3.997	49.61	0.199	2.366	180	0.02948	92,920	2.6018	0.4695
4.494	55.77	0.260	2.349	180	0.03503	117,400	2.6526	0.5445
4.495	55.77	0.233	2.369	180	0.03097	117,500	2.6527	0.4910
4.995	61.98	0.188	2.382	120	0.03325	145,000	2.6985	0.5217
5.495	68.19	0.238	2.370	120	0.03877	175,600	2.7400	0.5885
5.985	74.29	0.273	2.364	120	0.04130	208,300	2.7771	0.6160
5.994	74.38	0.271	2.358	120	0.04098	208,800	2.7777	0.6126
6.495	80.60	0.287	2.378	120	0.03992	245,100	2.8125	0.6012
6.990	86.75	0.322	2.377	120	0.04188	284,100	2.8445	0.6220
7.577	94.05	0.399	2.349	120	0.04952	333,800	2.8795	0.6948
7.585	94.15	0.379	2.375	120	0.04610	334,600	2.8800	0.6637

Table 11

y	$y-\bar{y}$	x	$x-\bar{x}$	$(x-\bar{x})(y-\bar{y})$	$(x-\bar{x})^2$
0.2240	-0.1156	1.9936	-0.2968	0.0343	0.0881
0.2261	-0.1135	1.9965	-0.2939	0.0334	0.0864
0.1801	-0.1595	1.9967	-0.2937	0.0468	0.0863
0.2330	-0.1066	2.0885	-0.2019	0.0215	0.0408
0.2987	-0.0409	2.1793	-0.1111	0.0045	0.0123
0.3012	-0-0384	2.2322	-0.0582	0.0022	0.0034
0.3556	+0.0160	2.2669	-0.0235	-0.0004	0.0006
0.3502	+0.0106	2.2683	-0.0221	-0.0002	0.0005
0.3345	-0.0051	2.2956	+0.0052	0	0
0.3522	+0.0126	2.2987	+0.0083	+0.0001	0.0001
0.3088	-0.0308	2.3001	+0.0097	-0.0003	0.0001
0.3923	+0.0527	2.3979	+0.1075	+0.0057	0.0116
0.3892	+0.0496	2.4004	+0.1100	+0.0055	0.0121
0.4161	+0.0765	2.4766	+0.1862	+0.0142	0.0347
0.4464	+0.1068	2.5437	+0.2533	+0.0271	0.0642
0.4953	+0.1557	2.6009	+0.3105	+0.0483	0.0964
0.4695	+0.1299	2.6018	+0.3114	+0.0405	0.0970
5.7732		38.9377		0.2832	0.6346

$\therefore \bar{y} = 0.3396 \qquad \therefore \bar{x} = 2.2904$

$\therefore$ The slope of the best least squares straight line $= \frac{0.2832}{0.6346} = 0.446$

The variable $y = 2 + \log_{10}k$ and the variable $x = 2 + \log_{10}d_i$. The mean values of y and x are denoted by $\bar{y}$ and $\bar{x}$. It is seen from Table 11 that the best least squares straight line through all the seventeen points has a slope of 0.446. Putting the equation to the straight line in the form $(y-\bar{y}) = m(x-\bar{x})$, it is seen that

$$2 + \log_{10}k = 0.3396 + 0.446\ (2 + \log_{10}d_i - 2.2904)$$

i.e. $$\log_{10}k = -1.7899 + 0.446 \log_{10}d_i \qquad \ldots\ldots (1)$$

In Table 12 are shown the results of calculating values of $2 + \log_{10}k$ from equation (1). The third column of this table gives the values of Δ, which is the difference between the experimental value of $2 + \log_{10}k$ given in Table 10 and the calculated value from equation (1). It is seen that four results are 0.02 or worse from the line (0.02 corresponds to a 5% error in k). These were rejected and another least squares calculation performed with the remaining thirteen points. The results are presented in Table 13. The equation to the best line through these points is,

$$\log_{10}k = -1.7846 + 0.433 \log_{10}d_i \qquad \ldots\ldots (2)$$

This equation was used to calculate values of $2 + \log_{10}k$, these values being included in Table 14. The differences Δ between these values and the experimental values are recorded in the third column of this table. It is seen that five points are 0.020 log unit or worse from the line of equation (2); these were now rejected. One point, corresponding to a cylinder diameter of 1.855 cm., which was more than 0.02 log unit from the line of equation (1) is now within tolerance and is now included in a final line fitting. The results are included in Table 15, from which it is seen that the best least quares straight line through the twelve remaining points has the following equation,

$$\log_{10}k = 1.7746 + 0.4061 \log_{10}d_i \qquad \ldots\ldots (3)$$

Table 12

$\log_{10} d_i$	Calculated value of $2 + \log_{10} k$	Δ
0.6018	0.4785	0.0090
0.6009	0.4781	0.0172
0.5437	0.4525	0.0061
0.4766	0.4226	0.0065
0.4004	0.3886	0.0006
0.3979	0.3875	0.0048
0.3001	0.3439	0.0351
0.2987	0.3433	0.0089
0.2956	0.3419	0.0074
0.2683	0.3297	0.0205
0.2669	0.3291	0.0265
0.2322	0.3136	0.0134
0.1793	0.2900	0.0087
0.0885	0.2495	0.0165
-0.0033	0.2087	0.0286
-0.0035	0.2086	0.0175
-0.0064	0.2073	0.0167

Table 13

y	$y-\bar{y}$	x	$x-\bar{x}$	$(x-\bar{x})(y-\bar{y})$	$(x-\bar{x})^2$
0.2240	-0.1282	1.9936	-0.3222	0.0413	0.1038
0.2261	-0.1261	1.9965	-0.3193	0.0402	0.1020
0.2330	-0.1192	2.0885	-0.2273	0.0271	0.0517
0.2987	-0.0535	2.1793	-0.1365	0.0073	0.0186
0.3012	-0.0510	2.2322	-0.0836	0.0043	0.0070
0.3345	-0.0177	2.2956	-0.0202	0.0004	0.0004
0.3522	0	2.2987	-0.0171	0	0.0003
0.3923	0.0401	2.3979	+0.0821	0.0033	0.0067
0.3892	0.0371	2.4004	+0.0846	0.0031	0.0072
0.4161	0.0639	2.4766	+0.1608	0.0103	0.0259
0.4464	0.0942	2.5437	+0.2279	0.0215	0.0519
0.4953	0.1431	2.6009	+0.2851	0.0408	0.0813
0.4695	0.1173	2.6018	+0.2860	0.0336	0.0818
4.5785		30.1057		0.2332	0.5386

$\therefore \bar{y} = 0.3522$ $\quad\quad$ $\therefore \bar{x} = 2.3158$

$\therefore$ The slope of the best least squares straight line $= \frac{0.2332}{0.5386} = 0.433.$

Table 14

$\log_{10} d_i$	Calculated value of $2 + \log_{10} k$	Δ
0.6018	0.4760	0.0065
0.6009	0.4756	0.0197
0.5437	0.4509	0.0045
0.4766	0.4218	0.0057
0.4004	0.3888	0.0004
0.3979	0.3877	0.0046
0.3001	0.3453	0.0365
0.2987	0.3447	0.0075
0.2956	0.3434	0.0089
0.2683	0.3316	0.0186
0.2669	0.3310	0.0246
0.2322	0.3160	0.0148
0.1793	0.2930	0.0057
0.0885	0.2537	0.0207
-0.0033	0.2140	0.0339
-0.0035	0.2139	0.0122
-0.0064	0.2127	0.0113

Table 15

y	$y-\bar{y}$	x	$x-\bar{x}$	$(x-\bar{x})(y-\bar{y})$	$(x-\bar{x})^2$
0.2240	-0.1260	1.9936	-0.3134	0.0395	0.0982
0.2261	-0.1239	1.9965	-0.3105	0.0385	0.0964
0.2987	-0.0513	2.1793	-0.1277	0.0066	0.0163
0.3012	-0.0488	2.2322	-0.0748	0.0037	0.0056
0.3502	+0.0002	2.2683	-0.0387	0	0.0015
0.3345	-0.0155	2.2956	-0.0114	0.0002	0.0001
0.3522	+0.0022	2,2987	-0.0083	0	0.0001
0.3923	+0.0423	2.3979	+0.0909	0.0038	0.0083
0.3892	+0.0392	2.4004	+0.0934	0.0037	0.0087
0.4161	+0.0661	2.4766	+0.1696	0.0112	0.0288
0.4464	+0.0964	2.5437	+0.2367	0.0228	0.0560
0.4695	+0.1195	2.6018	+0.2948	0.0352	0.0869
4.2004		27.6846		0.1652	0.4067

$\therefore \bar{y} = 0.3500 \qquad \therefore \bar{x} = 2.3070$

$\therefore$ The slope of the best least squares straight line $= \frac{0.1652}{0.4067} = 0.4061$

This line still excludes the same five results with errors of 0.02 + log unit and is within 0.02 log unit of all the twelve points accepted for Table 15. Consequently it was accepted as the best line through the points.

It can be seen from equation (3) that the relationship between k and d_i can be written as follows,

$$k = 0.0168\ d_i^{0.406} \qquad \ldots\ldots \quad (4)$$

The power on d_i, 0.406, differs by only 1.1/2% from the power 0.40 found by Eisenberg, Tobias and Wilke[32] in their work on heterogeneous reactions.

A similar series of nine experiments with cylinders of magnesium ranging in initial diameter from 2.476 cm. to 7.57 cm. was performed at 25°C, but the speed of rotation in each experiment was now 500 r.p.m. The volume of acid, initial concentration 0.0612 M, used in each experiment was 4,000 c.c., and care was taken that at the end of every experiment the partly spent acid was entirely removed from the large stainless steel reaction vessel and replaced by fresh acid in readiness for the next experiment. The relevant data obtained from the nine experiments are included in Table 16. The best straight line through the first six points (Reynold's Number from 17,750 to 103,300) obtained by plotting values of $(2 + \log_{10} k)$ versus $(2 + \log_{10} d)$ has a slope of 0.418, i.e., the unit rate constant is proportional to the radius raised to the power of 0.418, in quite good agreement with the findings of Eisenberg, Tobias and Wilke.

Table 16

Length of each cylinder = 3·95 cm.

Time t (sec)	Mean Diameter d (cm)	Mean Area A (sq. cm)	Weight Loss (gm)	k (cm/sec)	Reynold Number R_d	$2 + \log_{10} k$	$2 + \log_{10} d$
360	2.473	30.7	0.1199	0.01492	17,750	0.1738	2.3932
360	2.997	36.95	0.1602	0.01662	26,070	0.2206	2.4767
300	3.477	43.2	0.1550	0.01659	35,090	0.2198	2.5412
300	4.477	55.56	0.2360	0.01983	58,180	0.2973	2.6510
360	5.467	67.86	0.3524	0.02063	86,780	0.3145	2.7378
300	5.967	74.05	0.3380	0.02157	103,300	0.3338	2.7757
300	6.477	80.39	0.3847	0.02300	121,800	0.3617	2.8114
240	6.959	86.38	0.3429	0.02365	140,600	0.3738	2.8426
240	7.570	93,95	0.3866	0.02472	166,300	0.3931	2.8791

II(g) Larger Scale Experiments with and without Ultrasonic Irradiation.

In view of the fact that there appeared to be a considerable loss in power when an attempt was made to direct ultrasonic waves through the thick glass plate on to the flat lower surface of a magnesium cylinder, it was decided to dispense with the use of the conical glass reaction vessel and to use an arrangement whereby ultrasonic waves could be made to travel directly from the transducer disc through the acid medium and on to the exposed magnesium surface. For this purpose the heavy cylindrical transducer was carefully placed flat on the bottom of a 5-litre glass beaker containing three litres of acid solution. The magnesium cylinder, which was screwed on to the stirring shaft, was placed in the vertical position with its lower flat end directly over the transducer disc, about three inches from it. Care was taken with the adjustments of the positions of the magnesium cylinder and the transducer so that they were as nearly coaxial as possible. Figure 14 shows the arrangement in a typical experiment.

In actual experiments where ultrasonic waves were used, the generator was switched on before the cylinder of magnesium was lowered into position. The fountain effect produced on the liquid surface could then be used as a guide when adjusting the position of the cylinder. Before the latter was lowered into its final position, it was made to revolve at its predetermined speed.

The dimensions of the cylinder chosen for these experiments were length 3.95 cm, diameter 2.0 cm. Three experiments were performed without the use of ultrasonic waves at 25.5°C and the same number was performed with ultrasonic waves. Fresh hydrochloric acid (0.0659 N), volume 3,000 c.c., was used for each experiment.

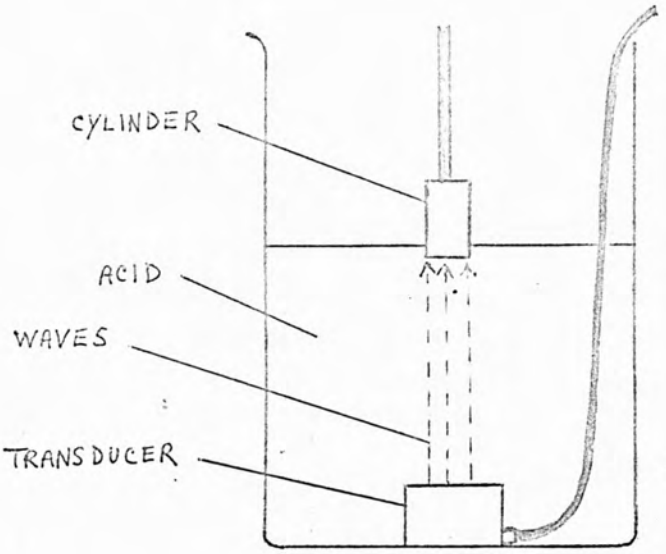
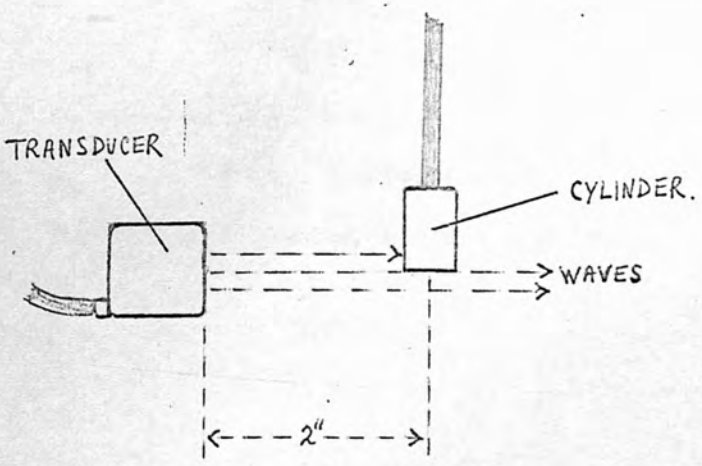


Figure 14

Figure 15



In each of these experiments the cylinder was rotated at 200 r.p.m. for a period of ten minutes. Only the lower flat end of the cylinder was left uncovered by collodion. At the end of the ten minute period, the cylinder was quickly removed from the acid, thoroughly washed with distilled water, dried and finally weighed. The weight loss was then deduced.

The weight losses in the three experiments without ultrasonic waves were respectively 0.0137 gm., 0.0143 gm., and 0.0140 gm., giving an average weight loss of 0.0140 gm. For the three experiments in which ultrasonic waves were used the weight losses were respectively 0.0318 gm., 0.0273 gm., and 0.0288 gm., giving an average weight loss of 0.0293 gm.

A pair of similar experiments, one with and one without ultrasonic waves, was performed at a temperature of 35.5°C. The loss in weight in the experiment without ultrasonic waves was 0.0164 gm., and the weight loss in the other experiment was 0.0432 gm.

With the data presented above we can calculate temperature coefficients of reaction, thus.

Equation (5) of Section II(b) is used to calculate the rate constants, it being assumed that the reaction between magnesium and 0.0659 N hydrochloric acid under the influence of ultrasonic waves follows first order kinetics. It has been pointed out in an earlier section that there is evidence that the reaction between the magnesium and acid of this concentration in the absence of ultrasonic waves is of the first order in acid concentration. For the experiments referred to above, V = 3,000 c.c., A = 3.14 sq.cm., t = 600 seconds, a = 2.404 grams.

At a temperature of 25.5°C in the absence of ultrasound,

$$k_{25.5} = \frac{2.303V}{At} \log_{10} \frac{a}{a - x}$$

$$= \frac{6,909 \times 0.00251}{1,884}$$

$$= 0.009204 \text{ cm/sec.},$$

and $$k_{35.5} = \frac{6,909 \times 0.00285}{1,884}$$

$$= 0.01045 \text{ cm/sec.}$$

At a temperature of 35.5°C with ultrasonic waves,

$$k_{25.5} = \frac{6,909 \times 0.00523}{1,884}$$

$$= 0.01918 \text{ cm/sec.},$$

and $$k_{35.5} = 0.02864 \text{ cm/sec.}$$

Therefore for reaction in absence of ultrasound, $\frac{k_{35.5}}{k_{25.5}} = \frac{0.01045}{0.009204} = 1.14$,

and for the ultrasonically influenced reaction, $\frac{k_{35.5}}{k_{25.5}} = \frac{0.02864}{0.01918} = 1.49$.

These temperature coefficients are within the range to be expected of a diffusion-controlled heterogeneous reaction, although the coefficient for the ultrasonically influenced reaction is significantly larger than that of the reaction not subjected to the influence of ultrasound.

Experiments in which ultrasonic waves were directed across the flat surface of a magnesium cylinder

Figure 15 shows the arrangement used, the cylinder rotating in an upright position and the transducer being just submerged in the dilute hydrochloric acid. Nine experiments were done at a temperature of 25.5°C, using 3,000 c.c. of fresh hydrochloric acid of initial concentration 0.0659N in each experiment. The same cylinder, length 4 cm. and diameter 2.0 cm., was used each time and it was rotated for 10 minutes at a speed of 200 r.p.m. in the acid with the ultrasonic generator on full power. Unfortunately, the reproducibility of the weight loss was not good, there being a variation from 0.0302 gram to 0.0460 gram. It was then decided to perform experiments with the cylinder rotating very close to the transducer (about 1 cm. away), as with this arrangement a proper alignment of the transducer disc and the exposed flat end of the cylinder, i.e. with the centre of the vertical disc in line with the centre of the horizontal cylinder surface, could be achieved.

Four experiments (in duplicate) were performed at a temperature of 35.5°C, using the same cylinder (4 cm. x 2 cm) with three litres of fresh 0.0659 N hydrochloric acid in each experiment. The cylinder was rotated at 200 r.p.m. for 10 minutes in each experiment, with the ultrasonic generator on full power. The weight loss figures for the four experiments were 0.0660 gm., 0.0650 gm., 0.0677 gm. and 0.0648 gm., giving an average weight loss of 0.0659 gm.

Five similar experiments performed at 25.5°C gave weight losses of 0.0564 gm., 0.0541gm., 0.0517 gm., 0.0575 gm. and 0.0536 gm., the average being 0.0547 gm.

A calculation similar to those performed in the previous sub-section gives $k_{35.5} = 0.04425$ cm/sec., and $k_{25.5} = 0.03674$ cm/sec., the assumption being made that the ultrasonically influenced reaction between the hydrochloric acid and magnesium is of the first order in acid concentration.

Therefore $$\frac{k_{35.5}}{k_{25.5}} = \frac{0.04425}{0.03674} = 1.205,$$

a temperature coefficient which is of a magnitude to be expected of a diffusion-controlled reaction.

II(h) Experiments to Test the Effect of Increases in the Stirring Speed of a Magnesium Cylinder on the Relative Rate of the Reaction between Magnesium and Dilute Hydrochloric Acid

At a given speed and temperature, the relative rate of the reaction between magnesium and hydrochloric acid is defined as the ratio of the rate of the reaction when subject to the action of ultrasonic waves to its rate when it is not subjected to ultrasound. The experimental arrangement for most of the experiments was the same as that described in the previous sub-section, with the cylinder very close (1 to 2 cm.) to the transducer disc; but for three of the experiments without ultrasound at a speed of 200 r.p.m., the experimental arrangement was that shown in Figure 14. However, it is assumed that the difference between the two arrangements will not alter the flow characteristics sufficiently to affect the rate of any diffusion-controlled reaction that may be taking place at the flat end of a magnesium cylinder. In each experiment 3,000 c.c. of fresh 0.0659 M hydrochloric acid was used. All experiments were performed with the acid at a temperature of 25.4°C. Speeds of revolution of 200, 800 and 1,150 r.p.m. were selected and in each experiment the cylinder was rotated in acid for ten minutes. Table 17 contains the data necessary to calculate the relative rates.

Table 17

[In all experimenta marked with an asterisk, ultrasonic waves were used].

Speed (r.p.m.)	Number of Experiments	Mean wt. loss in gm.
200	9	0.0159
200*	5	0.0547
800	2	0.0320
800*	5	0.0561
1,150	1	0.0429
1,150*	1	0.0627

For the purpose of calculating the relative rates, average values of the weight losses in ten minutes recorded in Table 17 were used. Thus at a stirring speed of 200 r.p.m.,

$$\text{Relative Rate} = \frac{\text{Rate at } 25.1/2^{\circ}\text{C with ultrasonics}}{\text{Rate at } 25.1/2^{\circ}\text{C without ultrasonics}} = 3.44$$

At a stirring speed of 800 r.p.m., Relative Rate = 1.75, and at a stirring speed of 1,150 r.p.m., Relative Rate = 1.46.

These relative rate figures show that an increase in the stirring speed of the cylinder has the effect of decreasing the relative rate of the reaction between magnesium and the dilute hydrochloric acid.

II(i) Use of Data to Check the Form of the Rate Equation for the Reaction between Magnesium and Hydrochloric Acid

The fact that the rate of evolution of hydrogen gas is so high in the reaction between magnesium and hydrochloric acid of concentration around 0.1 M at 25°C precludes accurate volume measurements of rates of reaction involving acid of concentration greater than this. Consequently we rely on weight-loss determinations to measure rates of reaction between the metal and acid of concentration greater than 0.1 M.

Provided the extent of reaction is only a few per cent, use can be made of the following method to check the form of the rate equation. Assuming a rate expression of the form $-\frac{dc}{dt} = k\frac{A}{V}c^n$, n being the order of the reaction, we can select two values of initial acid concentration c_1 and c_2 and write

$$\frac{-dc_1}{dt} = k\frac{A}{V} \cdot c_1^{\,n} \qquad \ldots\ldots \quad (1)$$

and

$$\frac{-dc_2}{dt} = k\frac{A}{V} \cdot c_2^{\,n} \qquad \ldots\ldots \quad (2)$$

Dividing (1) by (2), we have

$$\frac{\left(\frac{dc_1}{dt}\right)}{\left(\frac{dc_2}{dt}\right)} = \left(\frac{c_1}{c_2}\right)^n \qquad \ldots\ldots \quad (3)$$

Taking logarithms of both sides of equation (3) gives

$$\log_{10}\left[\frac{\left(\frac{dc_1}{dt}\right)}{\left(\frac{dc_2}{dt}\right)}\right] = n\log_{10}\left(\frac{c_1}{c_2}\right) \qquad \ldots\ldots \quad (4),$$

i.e.,

$$n = \log_{10}\left[\frac{\left(\frac{dc_1}{dt}\right)}{\left(\frac{dc_2}{dt}\right)}\right] \Big/ \log_{10}\left(\frac{c_1}{c_2}\right)$$

If the areas of the solid specimens are different in the two experiments, say A, sq.cm. and A_2 sq.cm., then equation (4) must be modified thus:

$$n = \log_{10}\left[\frac{A_2\left(\frac{dc_1}{dt}\right)}{A_1\left(\frac{dc_2}{dt}\right)}\right] \Big/ \log_{10}\left(\frac{c_1}{c_2}\right) \quad \ldots\ldots \quad (5).$$

In our case, we assume that the initial instantaneous rate $\frac{dc}{dt}$ is directly proportional to Δm, the weight loss in the finite time interval Δt from the start of the experiment. Therefore equation (4) becomes

$$n = \frac{\log_{10}\left(\frac{\Delta m_1}{\Delta m_2}\right)}{\log_{10}\left(\frac{c_1}{c_2}\right)} \quad \ldots\ldots \quad (6).$$

Table 18 includes data from some experiments on the magnesium-hydrochloric acid reaction covering a range in acid concentrations of 0.01647 M to 1.45 M. The volume of acid in each of these experiments was 3,000 c.c. No ultrasound was used in any of the experiments.

It will be noticed that the reaction is first order with respect to the hydrochloric acid concentration from the lowest concentration used, 0.01647 M, to about 0.16 M, for cylinders 4 cm. long and 2 cm. diameter revolving at 200 r.p.m., at a temperature of about 25°C. In agreement with this finding, it was shown in Section II(c) that, using the results of experiments in which rates were determined from gas volume measurements, the order of reaction in dilute acid (0.033 M) was one. Table 18 also shows that the apparent order of the reaction rises with increasing acid concentration, until at about 1 M hydrochloric acid it is about two. It is interesting to note that B. Roald and W. Beck,[48] who used weight-loss determinations on the curved surface of cylinder, discovered that the rates of reaction were directly proportional to the acid concentration,

Table 18

Speed r.p.m.	Temp. ^{o}C	Part of cylinder exposed	c_1 molar	c_2 molar	Time allowed for reaction (minutes)	Δm_1 (grams)	Δm_2 (grams)	n
200	25.3	Flat end 2 cm. diameter	0.01647	0.0659	10	0.004267	0.0162	0.96
200	25.3	Flat end 2 cm. diameter	0.0659	0.1647	10	0.0162	0.0404	1.00
200	25.5	Flat end 2 cm. diameter	0.1647	0.3295	5	0.01775	0.0525	1.56
200	25.3	Flat end 2 cm. diameter	0.3295	0.659	5	0.0517	0.1546	1.58
200	25.5	Flat end 2 cm. diameter	1.170	1.45	3	0.137	0.214	2.08

i.e., the reaction was first order, for the more dilute acid solutions up to a concentration about decimolar at low speeds of revolution (of a few hundred r.p.m.), the slope of the straight line on a logarithmic plot being unity. At higher speeds of revolution, however, the direct proportionality between rate and acid concentration extended to concentrations progressively larger than decimolar. They found that at a hydrochloric acid concentration of about 1.4 molar, all the rate versus acid concentration curves (one for each speed of revolution) converge, i.e., cylinder speed no longer affected the rate of reaction.

When a plot of rate versus acid concentration is not a straight line, it is doubtful whether values of n calculated by means of equation (4) or equation (5) have much significance, except perhaps to show that the overall reaction does not have a simple order. We shall have occasion to discuss this point in another section.

In Table 19 are included data and the calculated n values for some experiments in which the reaction between magnesium and hydrochloric acid was subjected to the action of ultrasonic waves. The experimental set up was such that the lower flat end of the revolving upright cylinder was directly over the transducer disc, about 1 cm. above it, the transducer lying flat on the bottom of the reaction vessel. In each experiment 3,000 c.c. of acid were used. There was a slight increase in temperature due to the conversion of sound energy into heat, amounting to about one centigrade degree in 5 minutes. The figures in the last column provide evidence that the reaction, when influenced by ultrasonic waves, is of the first order over the approximate concentration range of 0.3 M to 3 M. The range may extend beyond 3 M, but this cannot be checked at present because no experiments with acid of concentration greater than 3 molar were performed.

Table 19

Speed r.p.m.	Temp. ^{o}C	Part of cylinder exposed	c_1 molar	c_2 molar	Time allowed for reaction (minutes)	Δm_1 (grams)	Δm_2 (grams)	n
200	Initial 25.5	Flat end 2 cm. diameter	0.3295	0.659	5	0.2377	0.4887	1.04
200	Initial 25.5	Flat end 2 cm. diameter	0.659	1.170	3	0.2932	0.5079	0.96
200	Initial 25.5	Flat end 2 cm. diameter	1.170	1.45	3	0.5079	0.6170*	0.91
1,000	Initial 25.5.	Flat end 1 cm. diameter	1.440	2.88	3	0.1848	0.3712	1.01

[* Single result. All other weight-loss figures are averages of two or more experimental results].

II(j) The Effect of Speed of Rotation and Ultrasonic Waves on the Rate of the Reaction between Magnesium and More Concentrated Hydrochloric Acid

Roald and Beck[48], in their experimental study of the reaction between magnesium and hydrochloric acid solutions at a temperature of 25°C, found that beyond a concentration of about 1.4 M the rate was independent of the speed of rotation of the 1.1 cm diameter cylinders which they used. Below are included some of our experimental results obtained with cylinders 3.95 cm. long,, some of diameter about 2 cm. and others having a diameter of about 1 cm., and hydrochloric acid of concentrations of about 1.45 M, 1.9 M and 2.9 M at a number of temperatures. In each experiment 3,000 c.c. of acid were used. The reaction vessel was the large (10-litre) stainless steel bucket mentioned in Section II(a). In every experiment a cylinder was rotated in an upright position while well immersed in acid solution. The temperatures recorded are mean values, but in no experiment was there a change in temperature of more than two Centigrade degrees. The results marked with an asterisk in Table 20 are from repeat experiments, i.e. two experiments with the same cylinder.

An examination of the results in Table 20 shows that in no series of experiments did the rate of reaction cease to be dependent on the speed of rotation of the cylinders. Even with acid of concentration 2.89 M, an increase in stirring speed of the 1 cm. diameter cylinders at 25.5°C from 2,500 r.p.m. to 5,500 r.p.m. brought about an increase of 62.5%, based on average weight losses, in the rate of reaction at the flat ends of the cylinders. Again in the two experiments carried out with the curved surface of cylinders rotating in 1.45 M hydrochloric acid at 25.5°C,

Table 20

Time of Run (minutes)	Temp. °C	Part of Cylinder Exposed	Acid Concentration (Molar)	Weight Loss in Grams				
				At 200 r.p.m.	At 1,000 r.p.m.	At 2,500 r.p.m.	At 4,000 r.p.m.	At 5,500 r.p.m.
3	25.5	Flat bottom end d_i = 2 cm.	1.45	0.1661 0.1601	0.4056 0.3473* 0.4061 0.3549*	-	-	-
2	Average 23° for expt. at 200 r.p.m. Average 24° for expt. at 4000 r.p.m.	Curved surface d_i = 2 cm.	1.45	2.420	-	-	4.187	-
2	Average 13° for expt. at 200 r.p.m. Average 14° for expt. at 1,000 r.p.m.	Curved surface d_i = 2 cm.	1.45	1.310	1.675	-	-	-
5	25.5	Flat bottom end d_i = 1 cm.	1.441	-	-	0.1780 0.1822	0.2155 0.2280 0.2126	0.254 0.262 0.264
2	25.5	Flat bottom end d_i = 1 cm.	2.89	-	-	0.1631* 0.1526 0.1496*	0.2213 0.1784* 0.1806*	0.2613 0.2510 0.2440
5	15.5	Flat bottom end d_i = 1 cm.	1.455 for expts at 1000 r.p.m. 1.458 for expts at 5,500 r.p.m.		0.0727 0.0719 0.0674	-	-	0.1607 0.1625
2	4	Curved surface d_i = 2 cm	1.45	0.5921	1.0202	-	1.6524	-
2	6	Curved surface d_i = 2 cm		-	1.701	-	2.696	-

and which are more comparable to the experiments of Roald and Beck, an increase in stirring speed from 200 r.p.m. to 4,000 r.p.m. caused an incrase of 73% in the rate of the reaction.

The results in Table 21 show the combined effect of ultrasonic waves and speed of revolution on the reaction at the flat ends of small magnesium cylinders (diameter 1.0 cm). All the experiments were performed at an initial temperature of 25.5°C. In the experiments where ultrasound was used, the ultrasonic waves were directed upwards on to the exposed lower flat surface of each cylinder. The distance between the transducer disc and the exposed surface of the cylinder parallel to it was about 1 to 2 cm. in each experiment. Relative rates (defined in Section II(h)) included in Table 21 were calculated by using average weight losses. It is interesting to note that, for the reaction between the metal and 2.89 M hydrochloric acid with a cylinder speed of 5,500 r.p.m., the relative rate is virtually one, i.e. the application of ultrasound has no. further effect on the reaction. In both series of experiments the relative rates decrease with increase in cylinder speed (although with 1.441 M acid the relative rates at 4,000 and 5,500 r.p.m. are about the same), a trend that was noticed in Section II(h) with the results for much more dilute acid and rotational speeds lower than those used in the experiments quoted in Table 21.

Table 21

Concentration of acid (molarity)	Wt. losses in grams at 2,500 r.p.m.		Relative Rate	Wt. losses in grams at 4,000 r.p.m.		Relative Rate	Wt. losses in grams at 5,500 r.p.m.		Relative Rate
	Without ultrasound	With ultrasound		Without ultrasound	With ultrasound		Without ultrasound	With ultrasound	
2.89	0.1631, 0.1526 and 0.1496	0.1931, 0.1815 and 0.2099	1.26	0.2213, 0.1784 and 0.1806	0.2078, 0.2297 and 0.2208	1.13	0.2613, 0.251 and 0.244	0.2446, 0.2542 and 0,2438	0.98
1.441	0.1071, and 0.1094	0.1531, 0.1486 and 0.1423	1.37	0.2155, 0.228 and 0.2126	0.2781 and 0.2317	1.17	0.1525, 0.1572 and 0.1585	0.1866 and 0.1830	1.18

II(k) Experiments in Which the Diameters of the Magnesium Cylinders were Allowed to Decrease Appreciably

Experiments were performed to investigate the kinetics of the reaction between magnesium and hydrochloric acid of concentration about 1 M, in which the diameters of the cylinders were allowed to decrease appreciably. It seems likely from the evidence presented in Section II(i) that the reaction in 1 M hydrochloric acid is still controlled by convective-diffusive processes, so the methods described in Section III(d), using equations (23) and (26) for diffusion-controlled reactions, can be used provided, of course, that we are working within the Reynold's Number range of 1,000 to about 100,000 (an examination of Eisenberg, Tobias and Wilke's original plot suggests in fact that the range extends somewhat beyond 100,000). It is interesting to note that A.G. Loshkarev[49] has presented evidence pointing to the fact that the dissolution of magnesium (and zinc) in 5.5 M hydrochloric acid is controlled by the diffusion of hydrogen ion to the metal surface.

In one series of experiments at a temperature of about 25°C, one charging of 9,850 c.c. of 1.150 M hydrochloric acid was used, this acid being placed in the large 10-litre stainless steel reaction vessel, which was in a thermostat. The magnesium cylinder used in this series of experiments had an initial diameter of 4.984 cm. and length 2 cm. During a run it was rotated at 800 r.p.m., care being taken to ensure that it was well immersed in the acid and placed as centrally as possible inside the stainless steel vessel. The procedure adopted to obtain the necessary data was to allow the cylinder to rotate for a predetermined time in the acid, then to remove it so that it could be washed and dried before its diameter was carefully measured by a micrometer gauge. The collodion

protruding beyond the upper and lower edges of the cylinder was carefully cut away with a razor blade. Then the cylinder, rotating at 800 r.p.m. on the end of the shaft, was replaced in the acid and the procedure repeated. As the acid was progressively used up the time allowed for a run was increased. In this way series of values of the radius r, and the time t, were obtained for substitution into equations (23) and (26) of Section III(d).

Before use can be made of equations (23) and (26) of Section III(d) the value of a^2 must be calculated by means of the expression $a^2 = \frac{12.16\ VI}{\pi h \rho E}$. In this case we have

$V = 9{,}850$ c.c., $\pi = 3.142$, $h = 2.0$ cm., $\rho = 1.75$ gm/c.c.,

$E = 36.46$ gm., $I = c_t$ (the concentration where r = o).

The value of c_t is calculated as follows:

The weight of the cylinder initially = 68.319 gm.

This is equivalent to 204.8 gm. of hydrochloric acid.

As the weight of HCl in the solution initially was 413.0 gm., the amount theoretically left at the end = 413.0 = 204.8 = 208.2 gm., in a volume of 9,850 c.c.

$\therefore$ The concentration in gm/c.c., $c_t = \frac{208.2}{9{,}850} = 0.02114$.

$$\therefore\ a^2 = \frac{12.16 \times 9{,}850 \times 0.02114}{3.142 \times 2.00 \times 1.75 \times 36.46} = 6.315$$

Table 22 includes the values of radius r, and time t, for this series of experiments. Figure 16 shows a plot of r versus t. The slope of the curve of Figure 16 was drawn, according to the method of W.H. Pearlson and J.H. Simons[50], at three points corresponding to values of r of 2.355 cm., 2.029cm. and 1.872 cm., respectively. The values found for the slope were 0.0003933, 0.0003126 and 0.0002508 respectively.

Figure 16

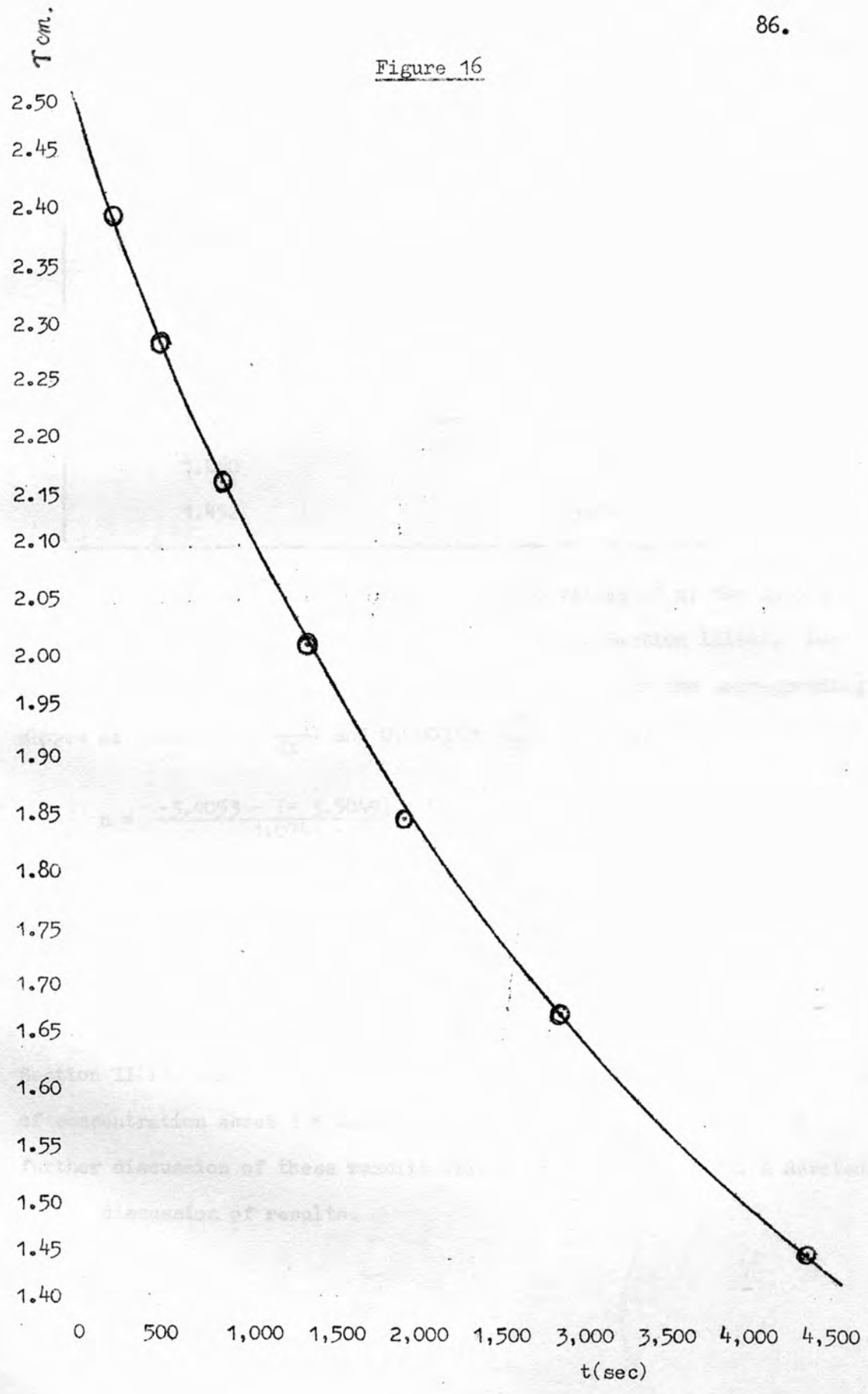

T cm.
2.50
2.45
2.40
2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
1.95
1.90
1.85
1.80
1.75
1.70
1.65
1.60
1.55
1.50
1.45
1.40
0
500
1,000
1,500
2,000
1,500
3,000
3,500
4,000
4,500
t(sec)

Table 22

Radius of cylinder r (cm)	Time in seconds
2.492	0
2.395	240
2.277	540
2.150	900
1.997	1,380
1.842	1,980
1.660	2,880
1.452	4,380

These data were then sued to calculate values of n, the apparent order of the reaction, by means of equation (26), Section III(d). For example, taking r_1 = 2.355 cm. and r_2 = 2.029 cm. with the corresponding slopes of 0.003933 ($= \frac{dr_1}{dt}$) and 0.0003126 ($\frac{dr_2}{dt}$), we have

$$n = \frac{-3.4053 - (-3.5049) + 0.4\{0.3073 - 0.3720\}}{1.0741 - 1.0183}$$

$$= 1.32$$

Again, with r_1 = 2.355 cm. and r_2 = 1.872 cm. with the corresponding slopes of 0.0003933 and 0.0002508, a similar calculation gives n = 1.90.

These values of n seem to support the conclusion reached in Section II(i), that the reaction between magnesium and hydrochloric acid of concentration about 1 M does not have a simple kinetic order. A further discussion of these results will be given in the section devoted to the discussion of results.

Table 23

Time of Experiment t, sec	r, cm	$\{r^{0.4}(r^2+a^2)\}^{-1}$	$\{r^{0.4}(r^2+a^2)^{\frac{3}{2}}\}^{-1}$	$\{r^{0.4}(r^2+a^2)^2\}^{-1}$	h	X_1	$X_{\frac{3}{2}}$	X_2
240	2.3950	0.05853	0.01686	0.004857	0.02425	0.0000230	0.00000.657	0.00000187
	2.4192	0.05771	0.01654	0.004741				
	2.4435	0.05696	0.01624	0.004630				
	2.4678	0.05618	0.01595	0.004526				
	2.4920	0.05540	0.01567	0.004420				
300	2.2775	0.06259	0.01846	0.005445	0.02937	0.0000237	0.00000691	0.00000201
	2.3069	0.06151	0.01802	0.005284				
	2.3362	0.06050	0.01764	0.005142				
	2.3656	0.05950	0.01725	0.004995				
	2.3950	0.05852	0.01686	0.004857				
360	2.1500	0.06732	0.02036	0.006154	0.03187	0.0000230	0.00000686	0.00000205
	2.1819	0.06609	0.01986	0.005972				
	2.2137	0.06490	0.01939	0.005790				
	2.2456	0.06371	0.01889	0.005604				
	2.2775	0.06259	0.01846	0.005445				
480	1.9975	0.07357	0.02291	0.007133	0.03812	0.0000224	0.00000686	0.00000211
	2.0356	0.07194	0.02224	0.006880				
	2.0737	0.07036	0.02158	0.006620				
	2.1119	0.06882	0.02097	0.006390				
	2.1500	0.06732	0.02036	0.006153				
600	1.8425	0.08065	0.02588	0.008303	0.03875	0.0000199	0.00000630	0.00000199
	1.8813	0.07879	0.02510	0.007998				
	1.9200	0.07703	0.02436	0.007703				
	1.9588	0.07525	0.02364	0.007420				
	1.9975	0.07357	0.02291	0.007133				
900	1.6600	0.09000	0.02988	0.009922	0.04562	0.0000168	0.000000564	0.00000184
	1.7056	0.08103	0.02884	0.009492				
	1.7512	0.08520	0.02783	0.009082				
	1.7969	0.08290	0.02684	0.008683				
	1.8425	0.08065	0.02588	0.008305				
1,500	1.4525	0.10224	0.03522	0.01213	0.05188	0.0000133	0.00000449	0.00000152
	1.5044	0.09900	0.03382	0.01155				
	1.5563	0.09590	0.03245	0.01097				
	1.6081	0.09283	0.03110	0.01042				
	1.6600	0.09000	0.02988	0.009922				

Data from the same series of experiments were substituted into equation (23) of Section III(d). Equation (23) was derived, of course, on the assumption that $k \propto r^{0.4}$, and this appears to be so for the experiments under discussion because the Reynold's Numbers are within the appropriate range (10^3 to about 10^5) according to Eisenberg, Tobias and Wilke. The integral was evaluated by means of Simpson's Rule, which with five ordinates (i.e. four strips) is

$$\int_{r_2}^{r_1} f(r)dr = \frac{h}{3}\left\{f_o + f_4 + 4\,(f_1 + f_3) + 2f_2\right\} \qquad \ldots\ldots \quad (1)$$

where h is the width of each strip and f_o, f_1, f_2, f_3 and f_4 are, respectively, the values of f(r) i.e., the ordinates at $r = r_2$, $r_2 + h$, $r_2 + 2h$, $r_2 + 3h$ and $r_2 + 4h$ $(=r_1)$. In our case $f(r) = \left\{r^{0.4}(r^2 + a^2)^n\right\}^{-1}$, where n is the order of reaction and, for this particular series of experiments, $a^2 = 6.315$. Therefore equation (23) becomes

$$X_n = \frac{1}{t}\int_{r_2}^{r_1} \left\{r^{0.4}(r^2 + a^2)^n\right\}^{-1} dr = \frac{h}{3t}\left\{f_o + f_4 + 4(f_1+f_3) + 2f_2\right\} \qquad \ldots\ldots \quad (2)$$

Values of X_n, with $n = 1, \frac{3}{2}$, and 2, respectively, were calculated by means of equation (2), values of t, r_2 and r_1 being taken from Table 22. The detailed results of these calculations are included in Table 23. The first four values of $X_{\frac{3}{2}}$ are quite constant (variation about 5%), but so are the first four values of X_1 (variation of about 6%); while the first four values of X_2 steadily rise from 0.0000187 to 0.0000211 (variation about 12%). In all cases, there is a steady fall in the X values from the fourth onwards. Therefore it appears, on the basis of the X values reported in Table 23, that the reaction does not have any of the orders 1, $\frac{3}{2}$ or 2.

In another series of experiments at a temperature of about 25°C, one charging of 3,000 c.c. of 1.166 M (initial concentration) hydrochloric acid was used in the ten-litre stainless steel reaction vessel, which was placed in a thermostat. Six experiments in all were carried out with a cylinder the initial diameter of which was 2.001 cm. and length 3.95 cm. During each experiment the cylinder was rotated at a speed of 1,000 r.p.m. The procedure adopted to obtain the necessary experimental data was similar to that described for the previous series of experiments. Values of radius r, and the corresponding times, t, so obtained are given in Table 24. The value of a^2, calculated by the formula $a^2 = \frac{12.16\ VI}{\pi\ h \rho\ E}$, is 0.9582.

Table 24

Radius of Cylinder (cm)	Time (sec)
1.0005	0
0.9370	150
0.8965	270
0.8565	390
0.8215	510
0.7890	630
0.7580	750

Figure 17 shows the curve obtained by plotting the values of r versus t from Table 24. Values of the slope, found by the method previously referred to, at three points correspondning to values of r of 0.977 cm., 0.879 cm. and 0.800 cm. were, respectively, 0.0004094, 0.0003229 and 0.0002623. These data were then used to calculate values of n by means of equation (26), Section III(d). Taking r_2 = 0.977 cm., and r_2 = 0.879 cm., the value found for n was 1.95; with r_1 = 0.977 cm. and r_2 = 0.800 cm., n was found to be 2.03. In this series of experiments, when the radius of the cylinder decreased from 0.977 cm. to 0.800 cm. the concentration of the acid decreased from about 1.1 M to approximately 0.9 M. The results of

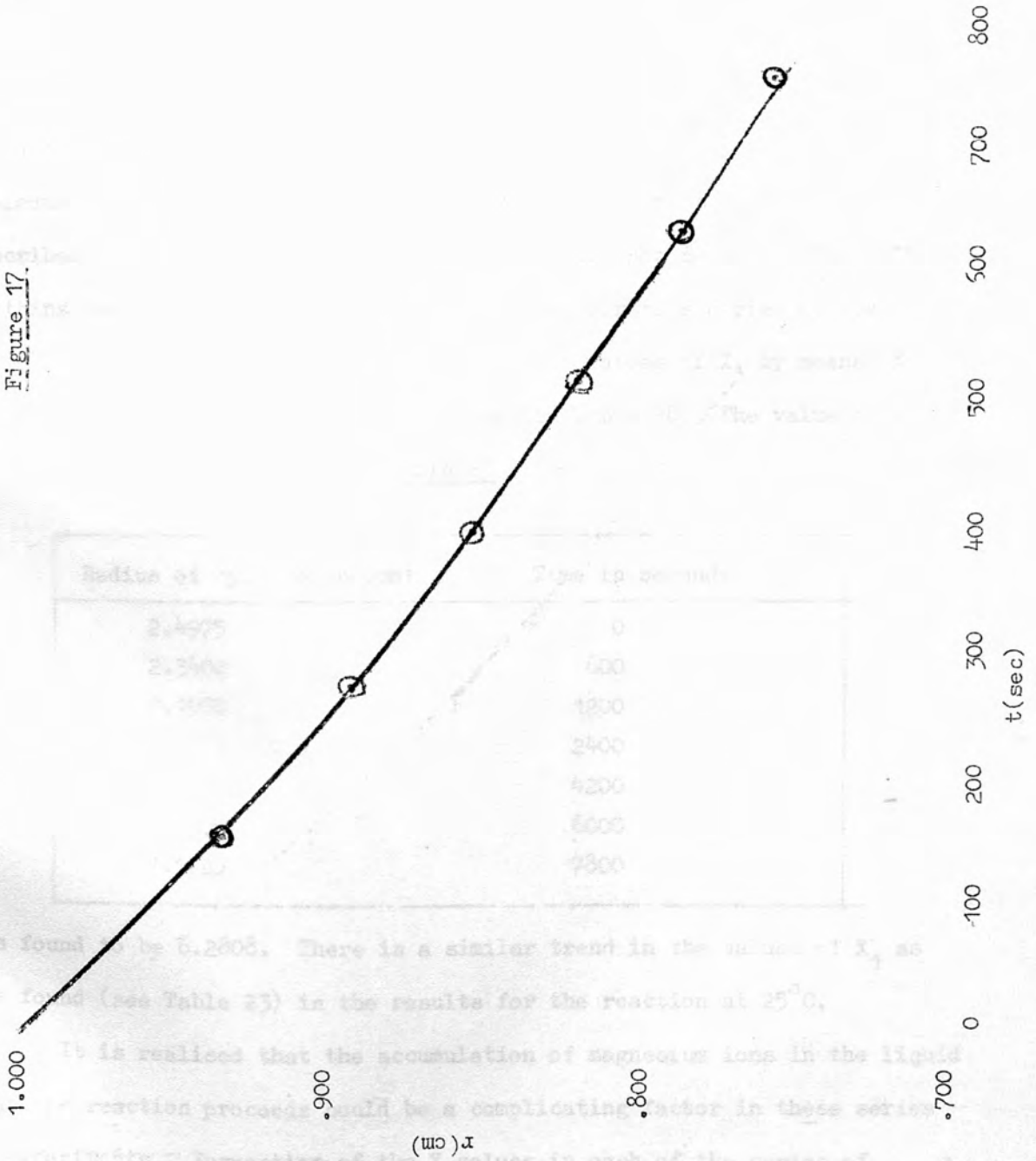


Figure 17.

the calculations by equation (26) referred to above indicate that in this fairly narrow concentration range the apparent order n of the reaction is about 2, in approximate agreement with the conclusion noted in Section II(i)

A series of experiments was also carried out at a temperature of about 15°C, one charging of 9,845 c.c. of initially 1.150 M hydrochloric acid being used in the ten-litre stainless steel reaction vessel, which was in a thermostat. The magnesium cylinder used in this series of experiments had a length of 2 cm., and an initial diameter of 4.995 cm. In each run the cylinder was rotated at a speed of 800 r.p.m. The procedure adopted to obtain the necessary data was the same as that described for the first series of experiments in this Section. Table 25 contains the values of radius, r, and time, t, for this series of six experiments. These data were used to calculate values of X_1 by means of equation (23) and the results are included in Table 26. The value of a^2

Table 25

Radius of cylinder r (cm)	Time in seconds
2.4975	0
2.3400	600
2.1950	1200
1.9362	2400
1.6325	4200
1.3900	6000
1.1725	7800

was found to be 6.2808. There is a similar trend in the values of X_1 as was found (see Table 23) in the results for the reaction at 25°C.

It is realised that the accumulation of magnesium ions in the liquid phase as reaction proceeds could be a complicating factor in these series of experiments. Inspection of the X values in each of the series of

experiments with about ten litres of acid, one series at 25°C and the other at 15°C, shows that, for all orders investigated, X_n (and hence k_n) falls over the experiment as a whole. This would support the idea that the change of medium affects the rate constant. If, however, the early results for X_n are looked at in Table 23, it is seen that X_1 is constant to $\pm$ 3% up to 1,380 seconds. $X_{\frac{1}{2}}$ over the same period of observations rises (and later falls), with a variation to 1,380 seconds of $\pm$ 2½ %, while the variation in X_2 over the same period is about $\pm$ 12%. Thus it is not possible, for the early part of the reaction, to distinguish between first order and three halves order as a best fit, and it is only when one considers the longer times which involve considerable alteration in the composition of the solution that X_2 becomes the more apparently true.

Table 26

Time of Experiment, t sec	r, cm	$\left\{r^{0.4}(r^2+a^2)\right\}^{-1}$	h	X_1
600	2.3400	0.06054	0.0394	1.521×10^{-5}
	2.3794	0.05920		
	2.4187	0.05790		
	2.4581	0.05663		
	2.4975	0.05539		
600	2.1950	0.06579	0.0363	1.528×10^{-5}
	2.2313	0.06443		
	2.2675	0.06310		
	2.3038	0.06180		
	2.3400	0.06054		
1,200	1.9362	0.07655	0.0647	1.531×10^{-5}
	2.0009	0.07367		
	2.0656	0.07093		
	2.1303	0.06830		
	2.1950	0.06579		
1,800	1.6325	0.09788	0.0759	1.416×10^{-5}
	1.7084	0.08774		
	1.7843	0.08382		
	1.8603	0.08009		
	1.9362	0.07655		
1,800	1.3900	0.10673	0.0606	1.334×10^{-5}
	1.4506	0.10278		
	1.5112	0.09898		
	1.5719	0.09535		
	1.6325	0.09188		
1,800	1.1725	0.12257	0.0544	1.383×10^{-5}
	1.2269	0.11835		
	1.2813	0.11431		
	1.3356	0.11045		
	1.3900	0.10673		

II(1) Tables of Results obtained from Weight-Loss Determinations for the Hydrochloric Acid/Magnesium Reaction

This set of tables contains the collected results for this reaction where there were usually only small changes in the composition of the medium; hence the rate constants k were calculated assuming mean cylinder diameters and mean acid concentrations and a first order reaction. As pointed out elsewhere, the latter assumption may not be justified over all the range of acid concentration investigated, but the values calculated here may be suitable for comparison purposes.

Table 27

Curved Surface Results with 2 cm. Diameter Cylinders

Temperature °C	Molarity of Acid	Rate 'Constant' k (cm/min)		
		200 r.p.m.	1,000 r.p.m.	4,000 r.p.m.
25 ± 1°	0.004		1.25	
	0.0659	0.55	1.28(4)	3.43
	1.17		3.13	
	1.45	2.67(2)	3.55	5.20
14 ± 1°	0.0659	0.35	0.89	2.28
	1.17		2.04	
	1.45	1.40(2)	1.97	3.34
	1.9		2.73(2)	3.93
	2.85		4.31	4.57(2)
5 ± 1°	0.065	0.27	0.65	1.65
	1.45	0.68	1.19	1.96
	1.9		1.53	2.46

The numbers in parentheses in Table 27 show the number of repeat experiments averaged.

Table 28

Temperature °C	Molarity of Acid	Radius (cm)	Rate 'Constant' k (cm/min)										
			200 r.p.m.	350 r.p.m.	400 r.p.m.	500 r.p.m.	650 r.p.m.	800 r.p.m.	1,500 r.p.m.	2,000 r.p.m.	2,500 r.p.m.	3,000 r.p.m.	4,000 r.p.m.
25.5	0.503	1.20 ± 0.025	1.01	1.23		1.32	1.46	1.54					
15.5	0.503	1.16 ± 0.05	0.78		1.00	1.00		1.22	1.47		1.86		
25	1.42	0.86 ± 0.1							2.63	2.90		4.18	5.09

Table 29

Temperature °C	Molarity of Acid	Radius (cm)	Rate 'Constant' k (cm/min)										
			200 r.p.m.	350 r.p.m.	400 r.p.m.	500 r.p.m.	650 r.p.m.	800 r.p.m.	1,500 r.p.m.	2,000 r.p.m.	2,500 r.p.m.	3,000 r.p.m.	4,000 r.p.m.
25.5	0.503	1.20	1.01	1.23		1.32	1.46	1.54					
15.5	0.503	1.16	0.77		0.99	1.00		1.22	1.48		1.87		
25	1.42	0.86							2.57	2.96		4.18	4.99

The values of k in Table 28 could be corrected for the variation in radius. If diffusive control were dominant $k \propto r^{0.4}$: if chemical control were dominant, $k \propto r^{0}$. Hence an approximate correction for these fairly concentrated acids can be made by correction the k values to a mean radius by using the relation $k_{obs} \propto r^{0.2}$. Strictly the relationship $k \propto r^{0.4}$ applies when k is a unit first order rate constant for diffusive control within the Reynolds Number range of 1,000 to about 100,000. The corrected k values are included in Table 29.

The results included in Tables 30 and 31 are from experiments in which the lower flat ends of cylinders were exposed to attack by hydrochloric acid.

Table 30

Temperature °C	Molarity of Acid	Rate 'Constant' k (cm/min)	
		200 r.p.m.	1,000 r.p.m.
25.5	0.0165	0.74(3)	
	0.0659	0.69(9)	
	0.165	0.61(3)	
	0.330	0.86(4)	
	0.669	0.96(4)	
	1.17	1.04(4)	
	1.45	1.26(6)	2.38(4)
5.4	0.330	0.45	

Table 31

Temperature °C	Molarity of Acid	Radius (cm)	Rate 'Constant' k (cm/min)								
			200 r.p.m.	800 r.p.m.	1,000 r.p.m.	1,150 r.p.m.	2,500 r.p.m.	3,200 r.p.m.	4,000 r.p.m.	5,500 r.p.m.	5,900 r.p.m.
25	1.45	1.0			1.46		2.62(2)		3.17(3)	3.75(4)	3.70
	1.90	1.0			1.77(4)						
	2.89	1.0		2.37	2.95		3.70	4.50	4.58		
15.5	1.45	1.0			0.99(4)					2.32(2)	
25	0.066	2.0	0.69(9)	1.32(2)		1.77					

II(m) Extension of Work to Acids other than Hydrochloric Acid, in Particular to Determine Chemical Rate Constants by Roller's Method[9]

A number of acids was chosen for investigation, ranging from acetic acid (thermodynamic dissociation constant of 1.75×10^{-5} at 25°C) to hydrochloric acid. Table 32 lists these acids together with the corresponding thermodynamic dissociation constants[51] at 25°C.

Table 32

Name of Acid	Thermodynamic Dissociation Constant
Acetic	1.75×10^{-5}
Formic	21.4×10^{-5}
Phenoxyacetic	67.5×10^{-5}
Citric	$K_1 = 73.0 \times 10^{-5}$
	$K_2 = 1.7 \times 10^{-5}$
	$K_3 = 0.041 \times 10^{-5}$
Salicylic	125.0×10^{-5}
Monochloracetic	150.0×10^{-5}
Benzenesulphonic	279.0×10^{-5}
Trichloracetic	$3,000.0 \times 10^{-5}$
Hydrochloric	Large

Experiments with 0.105 M Acetic Acid at 25°C

It has been pointed out in Section III(b) that Roller's method requires the determination of the overall rate constants at different speeds of revolution of the solid. Therefore it was decided to determine these constants for the reaction between the magnesium cylinder and the acetic acid at speeds of 200, 300 and 400 r.p.m. The experimental method adopted was to

follow the course of reaction by noting the volume of hydrogen gas evolved at definite intervals. In each experiment 400 c.c. of fresh 0.105 M acetic acid was used, and a different magnesium cylinder was used each time. The cylinders were all nominally 2 cm. diameter, but their diameters differed slightly. Each cylinder had a length of 3.95 cm. Table 33 summarises the results obtained in the experiments.

Table 33

Time in minutes	Volume in c.c.		
	Experiment at 200 r.p.m. Atmos. pressure = 761.8 m.m.	Experiment at 300 r.p.m. Atmos. pressure = 758.3 m.m.	Experiment at 400 r.p.m. Atmos. pressure = 758.8 m.m.
1	8.4*	7.5	-
2	13.4^{O}	14.3	14.7
3	15.7	20.7	22.2
4	20.4	27.1	29.7
5	25.0	33.2	37.1
6	29.6	39.4	44.0
7	34.0	45.4	50.9
8	38.4	51.1	57.7
9	42.6	56.8	64.3
10	47.0	62.3	70.6
11	51.1	67.8	77.2
12	55.2	73.2	83.5
13	59.2	78.4	89.6
14	63.1	83.7	95.6
15	67.0	88.9	98.6$^{\Delta}$
16	70.7	94.0	
17	74.5		
18	78.2		

* Read at 1.5 minutes

O Read at 2.5 minutes

Δ Read at 14.5 minutes

At a speed of 500 r.p.m., the rate of evolution of gas was too rapid for accurate measurement, the gas burette filling up with hydrogen in about eight minutes.

400 c.c. of 0.105 M acetic acid would liberate 529.1 c.c. of hydrogen gas at 25°C and (761.8 - 23.8) m.m. mercury pressure. Therefore for the experiment at 200 r.p.m., H_o = 521.9 c.c. The values in the first and second columns of Table 34 have been calculated using this value for H_o (i.e. using 1.5 min. as t_o).

Table 34

H_o-H_t	$\log_{10}(H_o-H_t)$	t (min.)
516.9	2.7134	1
514.6	2.7115	1.5
509.9	2.7075	2.5
505.3	2.7036	3.5
500.7	2.6996	4.5
496.3	2.6958	5.5
491.9	2.6919	6.5
487.7	2.6881	7.5
483.3	2.6842	8.5
479.2	2.6805	9.5
475.1	2.6768	10.5
471.1	2.6731	11.5
467.2	2.6695	12.5
463.3	2.6659	13.5
459.6	2.6624	14.5
455.8	2.6588	15.5
452.1	2.6552	16.5

Figure 18 shows a $\log_{10}(H_o-H_t)$ versus t plot, and the slope m of the straight line = - 0.00389(7). The mean initial diameter of the

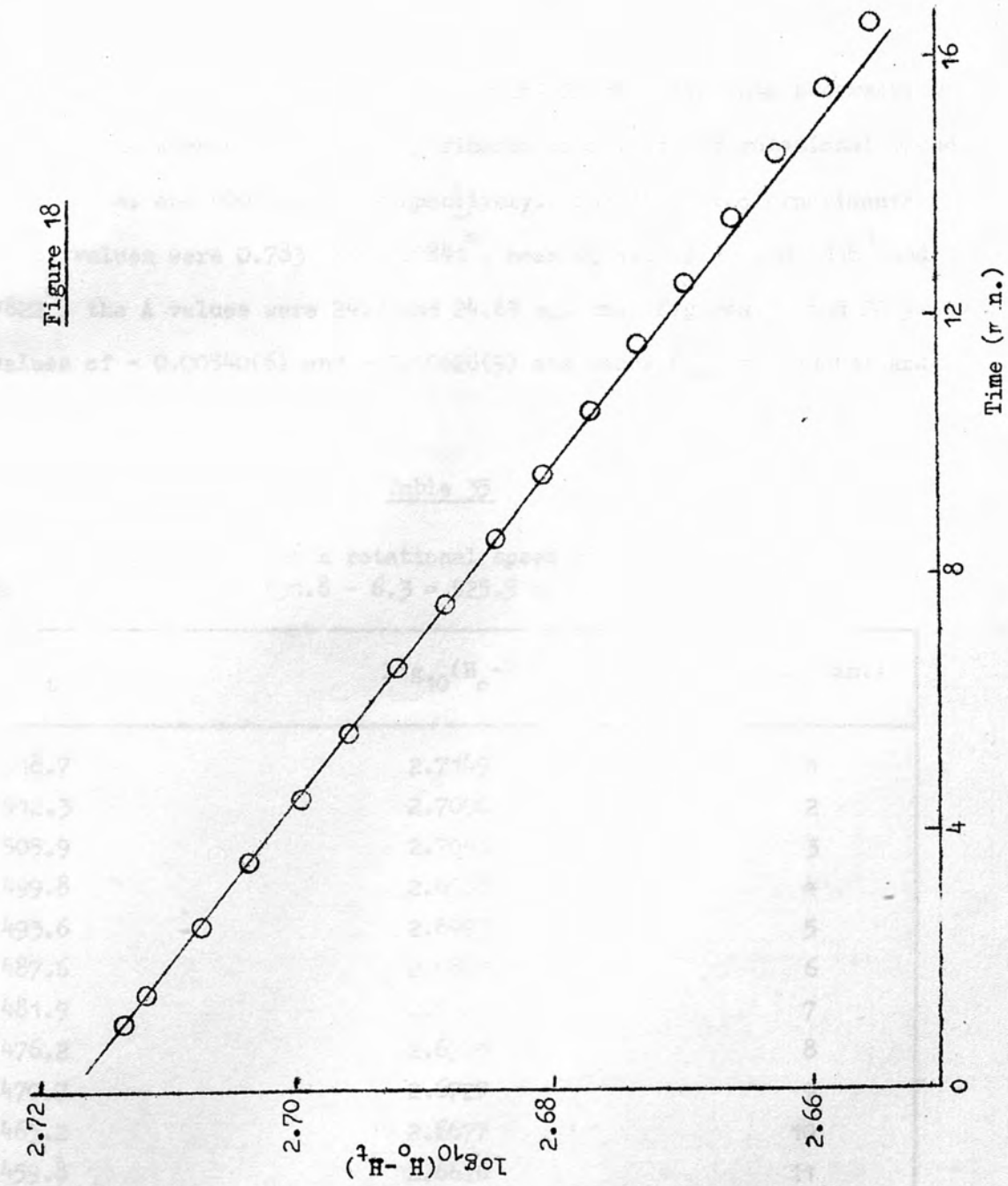


Figure 18

cylinder was 0.7750", while the average final diameter was 0.7745". Therefore the average area A of the curved surface = 24.41 sq.cm. Hence the observed first order rate constant k is given by,

$$k = \frac{2.303\ Vm}{A} = 0.144(2)\ \text{cm/min.}$$

Tables 35 and 36, and Figures 19 and 20 give the data necessary to calculate the k values for the experiments with cylinder rotational speeds of 300 r.p.m. and 400 r.p.m., respectively. For these two experiments mean d_i values were 0.783" and 0.7841", mean d_f values were 0.7816" and 0.7822", the A values were 24.7 and 24.69 sq. cm. Figures 19 and 20 yield m values of - 0.00540(6) and - 0.00626(9) and hence k_{300} = 0.192(3) and k_{400} = 0.229(1) cm/min.

Table 35

Experiment at a rotational speed of 300 r.p.m.
H_o = 531.8 - 6.3 = 525.5 c.c.

$H_o - H_t$	$\log_{10}(H_o - H_t)$	t (min.)
518.7	2.7149	1
512.3	2.7096	2
505.9	2.7041	3
499.8	2.6988	4
493.6	2.6993	5
487.6	2.6880	6
481.9	2.6829	7
476.2	2.6778	8
470.7	2.6727	9
465.2	2.6677	10
459.8	2.6626	11
454.6	2.6577	12
449.3	2.6525	13
333.1	2.6475	14
439.0	2.6425	15

Table 36

Experiment at a rotational speed of 400 r.p.m.

H_o = 531.4 - 13.5 = 517.9 c.c.

$H_o - H_t$	$\log_{10}(H_o - H_t)$	t (min.)
510.4	2.7079	1
502.9	2.7015	2
495.5	2.6950	3
488.6	2.6889	4
481.7	2.6827	5
474.9	2.6766	6
468.3	2.6705	7
462.0	2.6646	8
455.4	2.6584	9
449.1	2.6523	10
443.0	2.6464	11
437.0	2.6405	12
434.0	2.6375	12.1/2

Figure 19

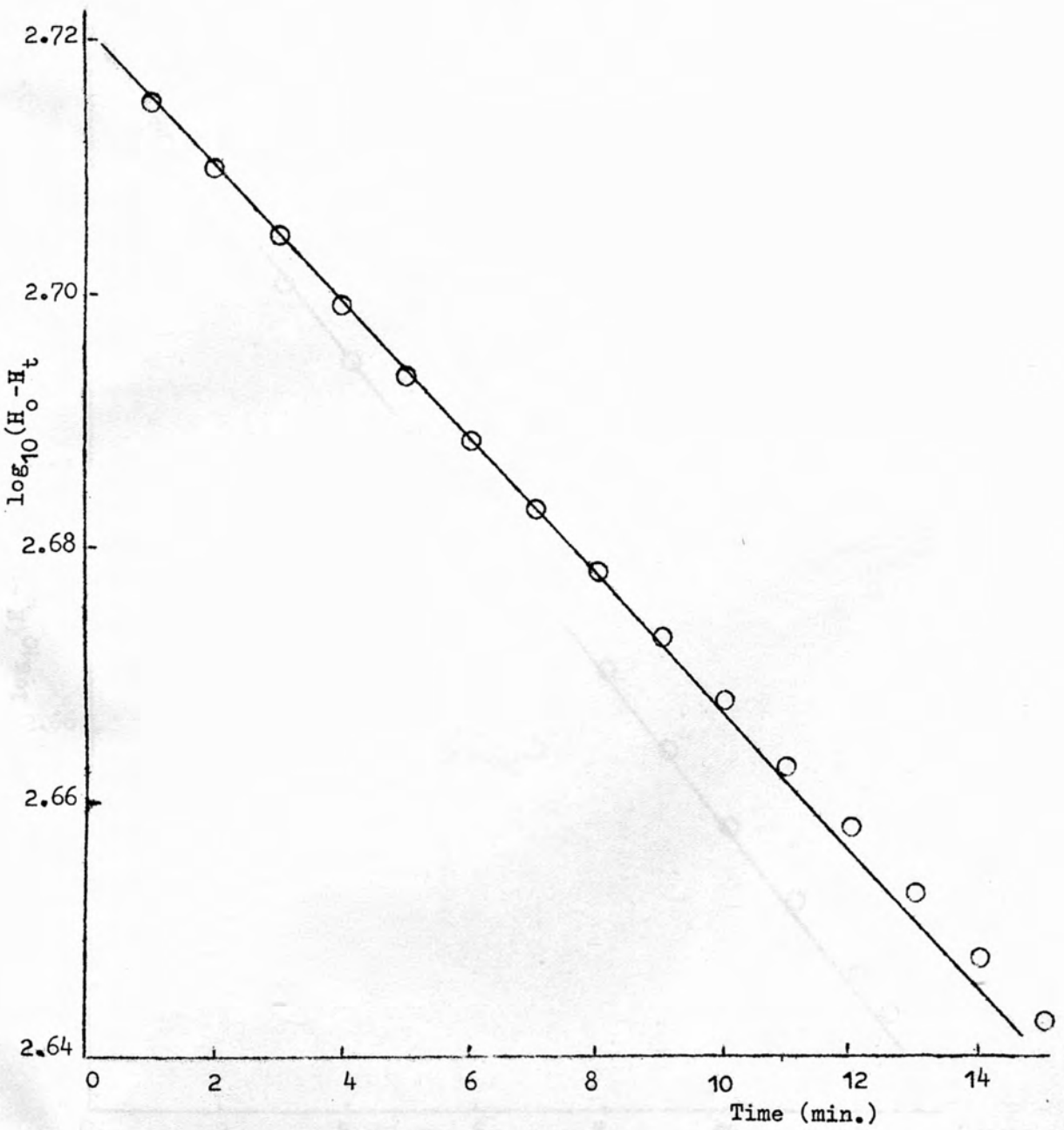
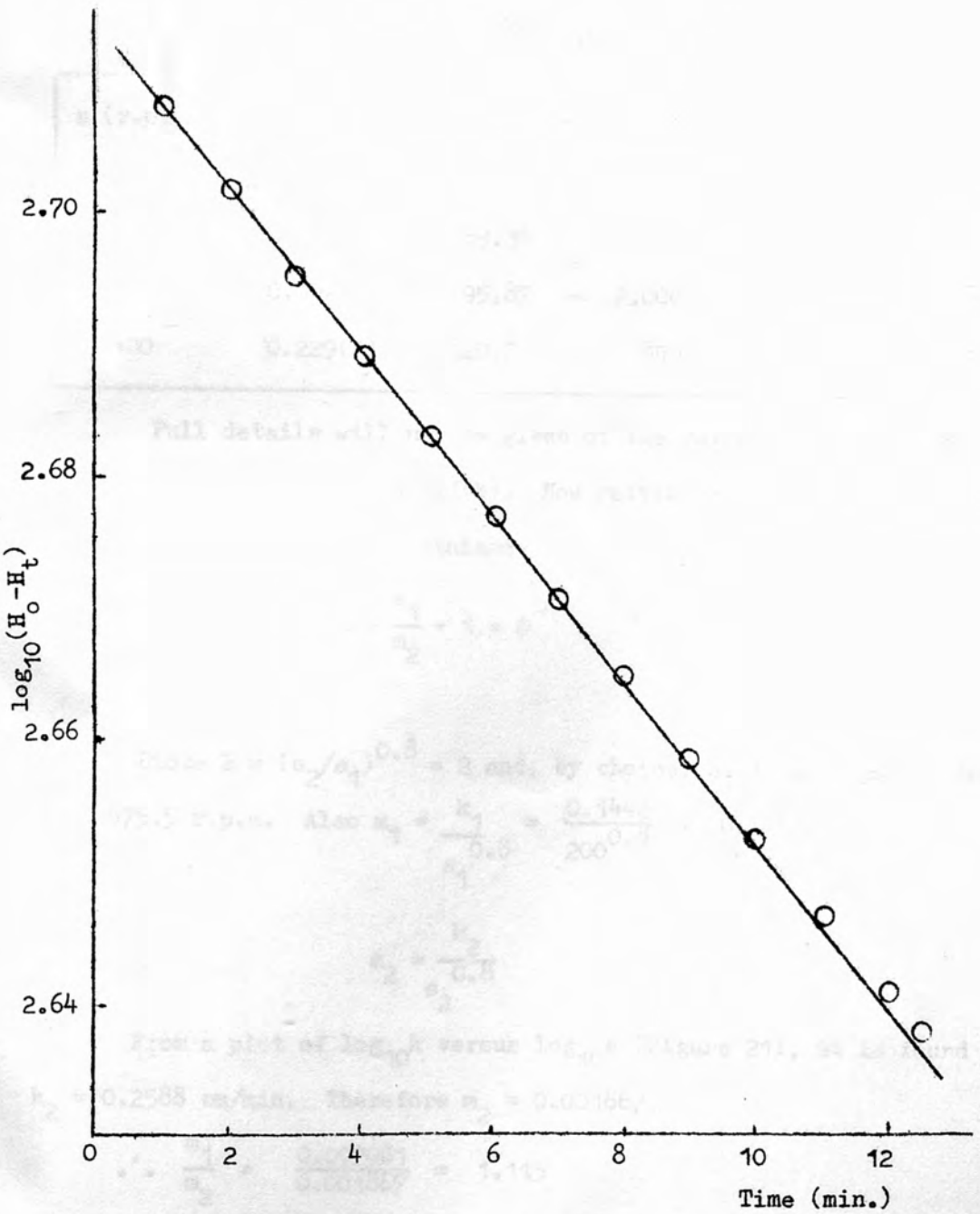


Figure 20



In Table 37 are included the data necessary to calculate values of k_c, the chemical rate constants.

Table 37

s (r.p.m.)	k (cm/min)	$s^{0.8}$	$\left(k/s^{0.8}\right) \times 10^3$	$\log_{10} s^{0.8}$	$\log_{10} k$
200	0.144(2)	69.31	2.081	1.8408	$\bar{1}.1590$
300	0.192(3)	95.87	2.006	1.9817	$\bar{1}.2840$
400	0.229(1)	120.7	1.898	1.0817	$\bar{1}.3600$

Full details will now be given of the calculation of k_c by means of equation (40), Section III(b). Now setting R = 2 in equation (47) of Section III(b), there is obtained:

$$Z^2 - \frac{m_1}{m_2} \cdot Z + \frac{m_1}{m_2} - 1 = 0 \qquad \ldots\ldots \quad (1).$$

Since $R = (s_2/s_1)^{0.8} = 2$ and, by choice, $s_1 = 200$ r.p.m., then $s_2 = 475.5$ r.p.m. Also $m_1 = \frac{k_1}{s_1^{0.8}} = \frac{0.1442}{200^{0.8}} = 0.002081$

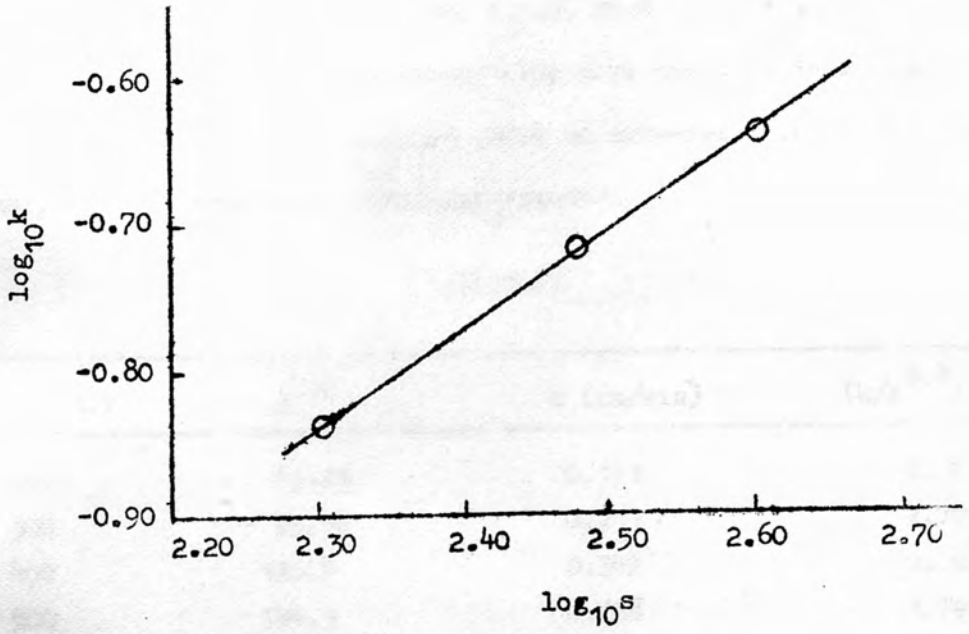
$$m_2 = \frac{k_2}{s_2^{0.8}}$$

From a plot of $\log_{10} k$ versus $\log_{10} s$ (Figure 21), it is found that $k_2 = 0.2588$ cm/min. Therefore $m_2 = 0.001867$.

$$\therefore \frac{m_1}{m_2} = \frac{0.002081}{0.001867} = 1.115$$

$\therefore$ Equation (1) becomes: $Z^2 - 1.113\,Z + 0.113 = 0$.

Figure 21



Solution of this equation shows that the only permissible value of Z is 0.115. Since $Z = 1 - m_2 x$ and $x = {}^1/_B$, it follows that

$$B = m_2/0.885 = 0.00211.$$

Equation (2) of Section III(b) gives $k_c = - Bs^{0.8} \log_e \left(1 - \frac{k}{Bs^{0.8}}\right)$. Substituting the data from the experiment at 200 r.p.m., in this equation there is obtained:

$$k_c = - 2.303 \times 0.00211 \times 69.31 \log_{10} \left(1 - \frac{0.1442}{69.31 \times 0.00211}\right)$$

$$= 0.629 \text{ cm/min.}$$

By corresponding substitutions k_c is found to be 0.608 cm/min at 300 r.p.m. and 0.585 cm/min at 400 r.p.m.

Experiments with 0.0260 M Acetic Acid

In view of the fact that the rate of evolution of hydrogen was so great at a rotational speed of 500 r.p.m. with 0.105 M acetic acid, it was decided to perform some experiments with more dilute acid so that the range of rotational speeds investigated could be extended. Table 38 contains a summary of the results of these experiments.

Table 38

s (r.p.m.)	$s^{0.8}$	k (cm/min)	$(k/s^{0.8}) \times 10^3$
200	69.23	0.191	2.76
300	95.98	0.211	2.20
400	120.8	0.242	2.00
500	144.3	0.258	1.79
600	167.0	0.367	2.20
700	188.8	0.376	1.99
800	210.1	0.414	1.97
885	227.8	0.441	1.94

If Roller's method is applicable, the values in the fourth column ought to decrease appreciably as the rotational speed increases, but this is not the case here. Therefore it was decided not to place reliance on these results for the calculation of k_c.

Experiments with 0.0254 M Monochloracetic Acid

400 c.c. of acid were used in each experiment, one with a cylinder speed of 200 r.p.m., one with a speed of 400 r.p.m., and a third experiment with a speed of 800 r.p.m. In each experiment a weight loss determination was carried out, and in each case it was found that considerably less hydrogen was produced than corresponded to the loss in weight of the magnesium cylinder, e.g. the weight loss in the experiment during which the cylinder rotated at 800 r.p.m. was 90.6 milligrams, whereas the volume of hydrogen produced was only 79.4 c.c. at 25°C and (758.0 - 23.8) m.m. mercury pressure. Under these conditions, if all the hydrogen displaced by 90.6 milligrams of magnesium from the acid appeared as gas, the total volume would have been about 94 c.c. Consequently it was suspected that some of the (nascent) hydrogen was used up in reducing the monochloracetic acid:

$$2[H] + Cl \cdot CH_2 \cdot COOH \longrightarrow CH_3 \cdot COOH + HCl$$

An aqueous solution of chloroacetic acid was prepared and a few drops of silver nitrate solution added; no precipitate formed, showing that silver chloroacetate must be fairly soluble. Next a few pieces of magnesium were placed in another clean test tube and a few c.c. of aqueous chloroacetic acid solution added. This reaction mixture was left for five minutes with hydrogen evolution. At the end of this time the mixture was filtered, and a few drops of silver nitrate solution were added to the filtrate. An immediate white precipitate formed. The usual tests showed this to be silver chloride. Hence nascent hydrogen reacts with chloroacetic acid to yield hydrogen chloride. The reduction was not mentioned in previous work on the monochloroacetic acid/magnesium reaction.

This demonstrates the reason for the discrepancy in the quantitative work. Neither result is correct for the rate of dissolution of magnesium in the chloroacid; the true result is probably between the two results.

Experiments with 0.0250 M Phenoxyacetic Acid

An experiment was performed with 400 c.c. of the phenoxyacetic acid and a magnesium cylinder of nominal diameter 2 cm. rotating at 800 r.p.m. The reaction was very slow as only 5.1 c.c. of gas was collected in the burette in 59 minutes and the cylinder lost 3.8 milligrams in weight. The cylinder surface was rather rough but bright. Because of the very slow rate of reaction, it was decided not to continue further with experiments using this acid.

Experiments with More Concentrated Acids

The reactions between magnesium cylinders and more concentrated acids (range from about 0.3 M to about 0.5 M) were followed by weight loss determinations. In each case it was assumed that the reaction was of the first order with respect to the concentration of the acid, although in the case of 0.2942 M formic acid it was experimentally demonstrated that at 25°C the reaction was of the first order throughout. Details of the experiment performed are given below.

Experiment to determine the Kinetic Order of the Reaction between 0.2942 M Formic Acid and Magnesium at a Temperature of 25°C

A magnesium cylinder of diameter 5.0 cm. was chosen for the experiment and its flat top end and all of its curved surface covered with collodion flexible. It was decided to rotate the cylinder at 500 r.p.m. with its exposed lower end just dipping below the surface of the formic acid

contained in a 600 c.c. beaker, which was placed in a thermostat maintained at 25°C. One charging of 200 c.c. of formic acid was used for the experiment, and the loss in weight of the cylinder was determined at intervals in the usual way, i.e. by carefully withdrawing it from the acid, followed by washing and drying before weighing. After each weighing, the cylinder was carefully re-introduced into the acid while rotating at 500 r.p.m. The procedure was repeated until the formic acid had been virtually exhausted, and there was no further loss in weight of the cylinder.

The solution capacity a of the acid = 0.200 x 12.16 x 0.2942 = 0.7152 gm. of magnesium. Let x denote the weight in grams of magnesium that has dissolved in time t minutes from the commencement of the reaction. Then a - x is proportional to c_t, the concentration of acid at time t. If the reaction is of the first order with respect to formic acid concentration, then a plot of $\log_{10}(a-x)$ versus t should give a straight line graph. The necessary data are included in Table 39. Figure 22 shows that a plot of $\log_{10}(a-x)$ does in fact give a straight line graph, thereby showing that the reaction, under the stated conditions, is of the first order with respect to the concentration of formic acid.

Table 39

t(min)	x (grams)	(a-x) grams	$\log_{10}(a-x)$
10	0.2267	0.4885	-0.3112
20	0.3748	0.3748	-0.4680
30	0.4888	0.2264	-0.6451
40	0.5614	0.1538	-0.8130
55	0.6248	0.0904	-1.0438
75	0.6705	0.0447	-1.3497
105	0.6722	0.0430	-1.3665

Figure 23 shows the graph obtained by plotting $\left(\frac{1}{a-x}\right)$ versus t. If the reaction between the magnesium and the formic acid were of the second order with respect to the acid concentration, such a plot should give a

Figure 22

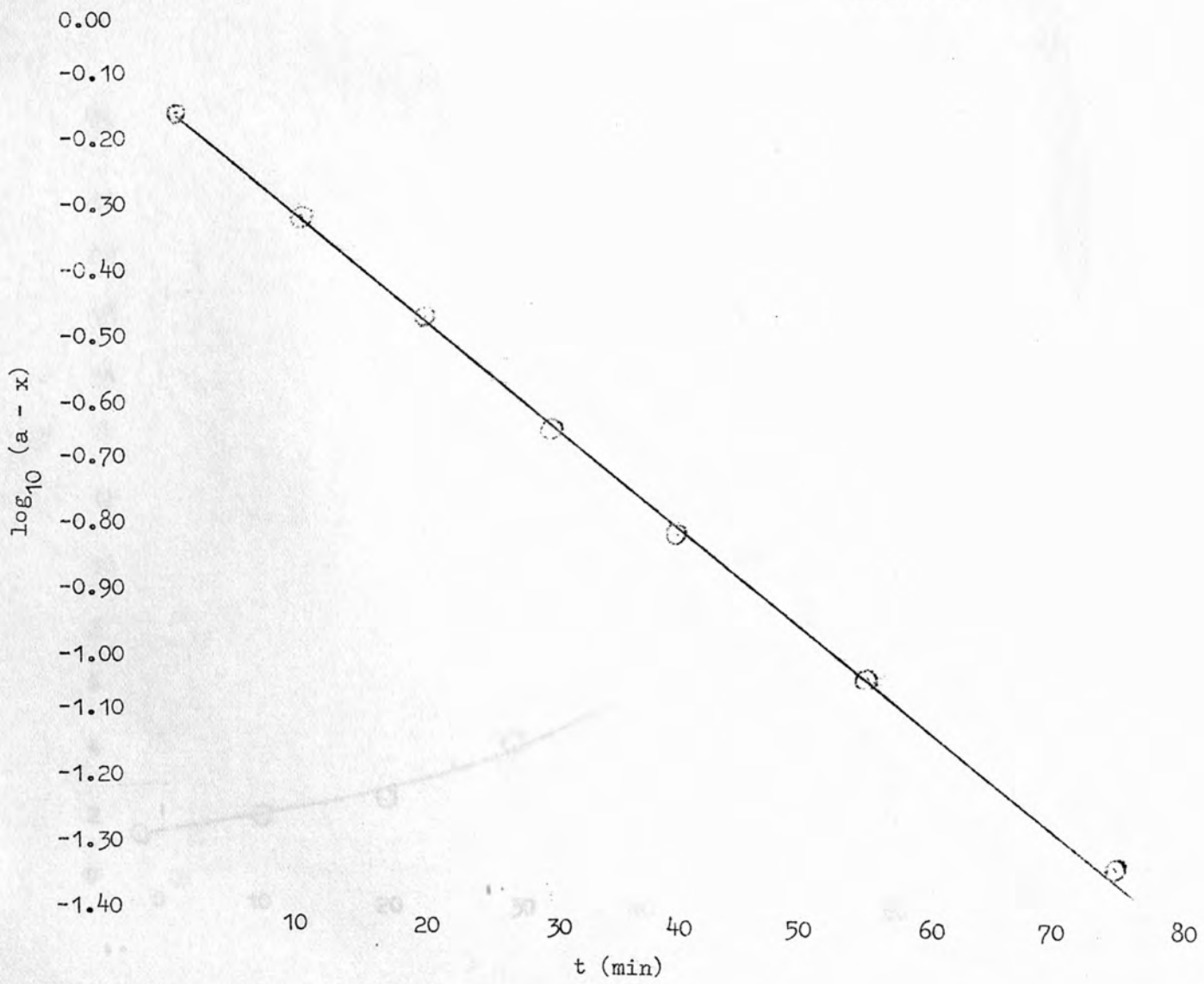
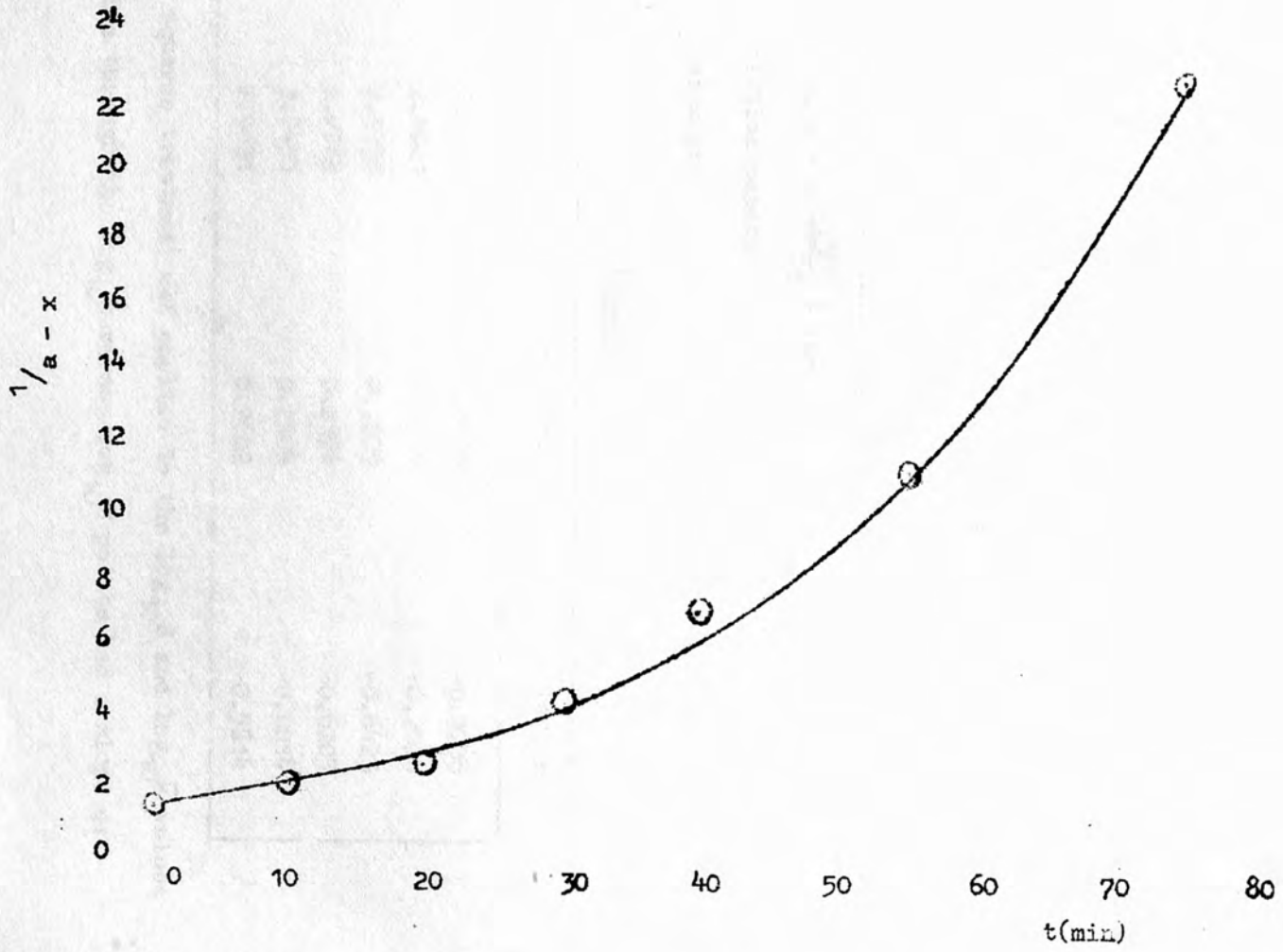

0.00
-0.10
-0.20
-0.30
-0.40
-0.50
-0.60
-0.70
-0.80
-0.90
-1.00
-1.10
-1.20
-1.30
-1.40
log10 (a - x)
10
20
30
40
50
60
70
80
t (min)

Figure 23



a straight line graph. The fact that the graph of Figure 23 is a curve shows that the reaction is lower than second order.

Determination of k_c for the Magnesium-Acetic Acid Reaction

Six experiments, in which the rate of reaction was followed by weight loss determinations, were performed at a temperature of 25°C with 0.5288 M acetic acid. One cylinder, length 3.95 cm. and initial nominal diameter 2 cm., was used for all the six experiments; but its speed of revolution was varied from experiment to experiment, the six speeds used being 300 r.p.m., 400 r.p.m., 500 r.p.m., 600 r.p.m., 700 r.p.m. and 800 r.p.m. The reaction vessel consisted of a 600 c.c. beaker clamped vertically in a thermostat. At the beginning of each experiment, 400 c.c of fresh acid were pipetted into the clean beaker. The reaction was allowed to proceed for three minutes in each run. Rate constants k were calculated by means of the formula $k = \frac{2.303\ V}{At} \log_{10} (\frac{a}{a - x})$. In all of these experiments the solution capacity a = 2.572 grams of magnesium. The calculated values of k are included in Table 40

Table 40

S r.p.m.	$\log_{10}S$	k cm/min	$\log_{10}k$
300	2.4771	0.1695	-0.7708
400	2.6021	0.1986	-0.7020
500	2.6990	0.2279	-0.6423
600	2.7782	0.2396	-0.6205
700	2.8451	0.2504	-0.6014
800	2.9031	0.2622	-0.5814

A least squares treatment was applied to the $\log_{10}S$ and $\log_{10}k$ values and the best line through the $\log_{10}k$ versus $\log_{10}S$ points had a slope of 0.4422.

Another series of four similar experiments was carried out at a temperature of 15°C, using 400 c.c. of fresh 0.5080 M acetic acid each time. The same cylinder, length 3.95 cm. and initial diameter 2.0 cm, was used throughout this sries of experiments. Its diameter was carefully measured before and after each experiment so that an average area A could be calculated for the curved reaction surface. The rotational speeds of the cylinder were, respectively, 300 r.p.m., 500 r.p.m., 800 r.p.m. and 1,200 r.p.m. In each experiment the reaction was allowed to proceed for 5 minutes. Values of the rate constant k, calculated by the formula quoted above, are included in Table 41.

Table 41

S r.p.m.	$\log_{10}S$	k cm/min	$\log_{10}k$
300	2.4771	0.09992	-1.0003
500	2.6990	0.1236	-0.9080
800	2.9031	0.1670	-0.7773
1,200	3.0792	0.1916	-0.7177

A least squares best line through the $\log_{10}k/\log_{10}s$ points has a slope of 0.4876.

For the purpose of calculating rate constants an average slope was used, viz. 0.465. This procedure could introduce an error if both transport control and chemical control were significant and if the two processes had very different activation evergies; but over a small temperature interval with reactions not having very different activation energies, this averaging is likely to smooth out individual errors. Average slopes were used similarly for formic acid, benzene sulphonic acid and hydrochloric acid. In this way the two weak acids were separated from the two strong ones.

In the case of acetic acid, taken as an example, the procedure adopted for calculating rate constants was as follows. The rate constant k at a speed of 750 r.p.m. at 15°C, this speed being the mid-point of the range of speeds used at this temperature, was calculated from the least squares straight line:

$$\log_{10}k = 0.4876 \times 2.8751 - 2.2108$$
$$= -0.8088.$$

The average slope result is thus, 0.8088 = 0.465 x 2.8751 - X, so the new intercept X = 2.1458. Hence the equation for calculating rate constants at 15°C is:

$$\log_{10}k = 0.465 \log_{10}S - 2.146 \quad \ldots\ldots \quad (1)$$

Similarly the equation for calculating k values at a temperature of 25°C was found to be:

$$\log_{10}k = 0.465 \log_{10}S - 1.917 \quad \ldots\ldots \quad (2)$$

Table 42 includes the values of k, calculated by means of equation (1), at the corresponding values of the experimental speed S.

Table 42

S r.p.m.	$\log_{10}S$	$\log_{10}k$	k cm/min	k_c cm/min
300	2.4771	-0.994	0.1014	0.250
500	2.6990	-0.891	0.1285	0.237
800	2.9031	-0.796	0.1599	0.255
1,200	3.0792	-0.714	0.1932	0.283

The values of k_c at 15°C, given in the last column of Table 42, were calculated by the procedure discussed in detail earlier in this Section. S_1 was chosen as 300 r.p.m., and with R = 2, S_2 = 713.5 r.p.m. $\log_{10}k_{713.5}$ was calculated, by means of equation (1), to be -0.819, so $k_{713.5}$ = 0.1517 cm/min. The value of the constant B was found to be 0.001192.

In Table 43 are included the values of k at the corresponding experimental speeds S, calculated by means of equation (2). The values of k_c in the last column of this table were calculated by the procedure

Table 43

S r.p.m.	$\log_{10}S$	$\log_{10}k$	k cm/min	k_c cm/min
300	2.4771	-0.765	0.1718	0.421
400	2.6021	-0.707	0.1963	0.398
500	2.6990	-0.662	0.2177	0.400
600	2.7782	-0.625	0.2372	0.409
700	2.8451	-0.594	0.2547	0.420
800	2.9031	-0.567	0.2710	0.413

of Section III(b). Taking S_1 = 300 r.p.m. and R = 2, S_2 = 713.5 r.p.m. Equation (2) gave a value of -0.590 for $\log_{10}k_{713.5}$, so $k_{713.5}$ = 0.257 cm/min. The calculated value of B was 0.002022.

The average value of k_c at a temperature of 15°C is 0.256 cm/min and the average at a temperature of 25°C is 0.413 cm/min., giving a temperature coefficient of · 1.60.

Determination of k_c for the Magnesium-Formic Acid Reaction

Three experiments similar to those described in the last section were carried out with 0.2923 M formic acid at 15°C. The single cylinder used had an initial diameter of 2.403 cm. Speeds of revolution used, one in each experiment, were 200, 500 and 800 r.p.m. In each experiment the reaction was allowed to proceed for 10 minutes. Values of the rate constant k, calculated by means of the integrated form of the first order equation, are included in Table 44.

Table 44

S r.p.m.	$\log_{10}S$	k cm/min	$\log_{10}k$
200	2.3010	0.1883	-0.7251
500	2.6990	0.3026	-0.5191
800	2.9031	0.4636	-0.3338

The best straight line through the $\log_{10}S$ versus $\log_{10}k$ points has a slope of 0.6314.

Six similar experiments were performed at a temperature of 25°C with 0.2937 M formic acid. This time, however, three cylinders were used. They each had the same length, 3.95 cm., but their diameter differed slightly, although they were all nominally 2.5 cm. diameter cylinders. The time allowed for the reaction in each experiment was 10 minutes. In Table 45 are included values of the rate constant k, calculated by the first order equation, for the six experiments together with the corresponding speeds of revolution.

Table 45

S r.p.m.	$\log_{10}S$	k cm/min	$\log_{10}k$
200	2.3010	0.2239	-0.6500
300	2.4771	0.2897	-0.5380
400	2.6021	0.4016	-0.3963
500	2.6990	0.3774	-0.4232
650	2.8129	0.4915	-0.3085
800	2.9031	0.5708	-0.2435

The slope of the best least squares straight line through the $\log_{10}S/\log_{10}k$ points has a slope of 0.6591.

For the purpose of calculating values of k_c at the two temperatures, the average of the two slopes, 0.645, was used. The same procedure as that in the

previous section was followed, and this led to the following two equations for calculating values of k:

At 15°C ..... $\log_{10}k = 0.645 \log_{10}S - 2.226$ ..... (3)

At 25°C ..... $\log_{10}k = 0.645 \log_{10}S - 2.125$ ..... (4)

In Table 46 are included the values of k calculated by equation (3).

Table 46

S r.p.m.	$\log_{10}S$	$\log_{10}k$	k cm/min	k_c cm/min
200	2.3010	-0.7419	0.1812	0.719
500	2.6990	-0.4851	0.3273	0.740
800	2.9031	-0.3535	0.4431	0.877

The values of k_c in the last column were calculated as in the last section, with a calculated value of B of 0.002674.

Table 47 includes the values of k calculated by equation (4).

Table 47

S r.p.m.	$\log_{10}S$	$\log_{10}k$	k cm/min	k_c cm/min
200	2.3010	-0.6409	0.2286	-
300	2.4771	-0.5273	0.2970	0.947
400	2.6021	-0.4466	0.3576	0.949
500	2.6990	-0.3841	0.4130	0.994
650	2.8129	-0.3107	0.4890	1.078
800	2.9031	-0.2525	0.5591	1.165

The calculated value of the constant B used to calculate the values of k_c in the last column is 0.003298.

Experiments with Benzenesulphonic Acid at 15°C

A similar series of three experiments at rotational speeds of 200, 500 and 800 r.p.m. respectively was performed with 0.4191 M benzenesulphonic acid.

The same cylinder, of initial diameter 2.306 cm and length 3.95 cm., was used in all of the three experiments. As a reaction vessel the same 600 c.c. glass beaker as was used in the previous series of experiments was used. 400 c.c. of fresh 0.4191 M acid were placed in the beaker at the beginning of each experiment. The time allowed for each experiment was five minutes. First-order rate constants were calculated by means of the integrated form of the first-order rate equation, and it was found that the best straight line through the $\log_{10}k$ versus $\log_{10}S$ points had the equation

$$\log_{10}k = 0.3464 \log_{10}S - 1.124 \quad \ldots\ldots \quad (2)$$

With S_1 = 300 r.p.m., S_2 = 713.4 r.p.m. By means of equation (2) k_1 = 0.5426 cm/min. and k_2 = 0.7325 cm/min. The value found for B was 0.007367. Equation (2) was used to calculate k_3, the overall rate constant at the intermediate speed of 500 r.p.m., giving a value of 0.6476 cm/min. The value found for k_c, using the value of 0.6476 cm/min. for k_3 in equation (40), Section III(b), was 1.00 cm/min.

Experiments with Benzenesulphonic Acid at 25°C

Four experiments were carried out with benzenesulphonic acid of initial concentration 0.3994 M at a temperature of 25.5 $\pm$ 1.5°C. The same 600 c.c. glass beaker as that in the previous series of experiments was used as the reaction vessel, and 400 c.c. of fresh acid were placed in it at the beginning of each experiment. Three different cylinders each of nominal

diameter of 2.5 cm. were used. Their diameters were measured both before and after experiments and mean values used in calculating the areas of the curved surfaces. Each cylinder had a length of 3.95 cm. The flat end surfaces of each cylinder were adequately covered with collodion flexile before commencing an experiment. Speeds of revolution used were 200 r.p.m., 350 r.p.m., 500 r.p.m. and 800 r.p.m., respectively. Each experiment was allowed to proceed for three minutes, except for the one in which the cylinder rotated at 200 r.p.m., which was allowed to run for ten minutes. The weight losses recorded were used to calculate first-order rate constants by means of the integrated form of the first-order rate equation, and the best straight line through the points obtained by plotting values of $\log_{10}k$ versus $\log_{10}S$ has the equation

$$\log_{10}k = 0.375 \log_{10}S - 0.9533 \qquad \ldots\ldots \quad (2)$$

In order to calculate the value for B, S_1 was chosen to be 300 r.p.m. so that S_2 = 713.4 r.p.m. By means of equation (2), it was found that k_{300} = 0.9435 cm/min. and $k_{713.4}$ = 1.309 cm/min., so that, by the usual procedure, B was found to have a value of 0.01229. Making use of equation (40), Section III(b), with k_{500} calculated by means of equation (2), k_c was found to have a value of 1.84 cm/min.

Experiments with Salicylic Acid

As this acid has a limited solubility at 25°C, a relatively dilute solution of molarity 0.0144 was used. Experiments were conducted with magnesium cylinders of nominal diameter 2 cm.; a micrometer screw gauge was used to measure their diameters accurately before commencing the experiments. Cylinder rotational speeds used were 200 rp.m., 400 r.p.m. and 800 r.p.m. The reaction vessel used in these experiments was the same

500 c.c. glass conical flask as that mentioned in the previous series of experiments. The course of the reaction was followed by noting the volume of hydrogen gas in the gas burette at definite intervals of time. In each experiment 400 c.c. of fresh salicylic acid solution were used.

First-order rate constants, k, for each experiment were obtained from plots of values of $\log_{10}(H_o - H_t)$ versus values of time. The best straight line through the $\log_{10}k$ versus $\log_{10}s$ points has the equation

$$\log_{10}k = 0.300 \log_{10}s - 1.343 \quad \ldots\ldots (1).$$

For the purpose of calculating the value of B, of equation (40), Section III(b), s_1 was chosen to be 300 r.p.m., so that $s_2 = 713.4$ r.p.m. From equation (1) it was found that $k_1 = 0.251_2$ and $k_2 = 0.325_8$ cm./min., and these values enabled the value of B to be calculated as 0.00371. k_3 at an intermediate speed of 500 r.p.m. was calculated by equation (1) to be 0.292_9 cm./min., and this value was used to calculate a value for k_c by means of equation (40), Section III(b). The value found for k_c was 0.42_4 cm./min.

Experiments with Citric Acid

A series of five experiments with citric acid of initial concentration 0.4684 M was performed at 15°C with cylinder rotational speeds of 300, 500, 800, 1,500 and 2,500 r.p.m., respectively. The reaction vessel was a 600 c.c. beaker and 400 c.c. of fresh acid was used in each experiment. The same cylinder, initial diameter 2.342 cm. and length 3.95 cm., was used in all the experiments, its curved surface being exposed to the acid. Each experiment was allowed to proceed for five minutes, and the weight loss in this time was measured. First-order rate constants were calculated for each speed of revolution

by means of the integrated form of the first-order rate equation. The best straight line through the $\log_{10}k$ versus $\log_{10}S$ plot has the equation

$$\log_{10}k = 0.175 \log_{10}S - 1.71 \quad \ldots\ldots \quad (1)$$

In order to calculate the value of the constant B, S_1 was chosen to be 300 r.p.m. Therefore S_2 = 713.4 r.p.m. By means of equation (1), it is found that k_{300} = 0.05290 cm/min. and $k_{713.4}$ = 0.06155 cm/min. By the usual procedure, it is found that B = 0.001142. The value of k_c, the chemical rate constant, was calculated at an intermediate speed of 500 r.p.m., the corresponding value of k_{500} being calculated by means of equation (1). As a results, k_c = 0.0713 cm/min.

A similar series of five experiments was carried out at 25 $\pm$ 1°C, with citric acid solution of initial concentration 0.4726 M, at the same cylinder speeds as for the previous series of experiments. The same 600 c.c. beaker was used and 400 c.c. of fresh acid placed in it at the beginning of each experiment, care having been taken to ensure that the beaker was clean and dry after the previous experiment. The same cylinder, of initial diameter 2.418 cm. and length 3.95cm., was used throughout this series of experiments. Each experiment was allowed to proceed for five minutes, except for the one at a speed of 2,500 r.p.m., which was allowed to proceed for three and a half minutes. First-order rate constants were calculated in the usual way from the weight losses, and the best straight line through the $\log_{10}k$ versus $\log_{10}S$ points has the equation

$$\log_{10}k = 0.1125 \log_{10}S - 1.174 \quad \ldots\ldots \quad (2)$$

For the purpose of calculating the value of B, S_1 was chosen to be 300 r.p.m., so that S_2 = 713.4. Substitution of these values in equation (2) gave k_{300} = 0.1273 cm/min. and $k_{713.4}$ = 0.1404 cm/min. By the usual procedure, B was found to have a value of 0.003921. The value of k_c was calculated by substituting the value of k_{500}, found by means of equation (2), in equation (40), Section III(b). As a result, the value of k_c was found to be 0.154 cm/min.

SECTION III

General Considerations

III(a) Change of Control and Shift of Control in Heterogeneous Reactions.

Following Bircumshaw and Riddiford[13a], we shall term an alteration in the dependence of the observed rate constant k_1 of a heterogeneous reaction upon the rate constants k_c or k_T of the primary processes as a shift of control. Such an alteration may bring about a change in the rate determining step, for example from transport control (Van Name and Hill's class (a)) to the intermediate type of control (Van Name and Hill's class (c)). Again using the terminology of Bircumshaw and Riddiford, we shall describe a change in the rate determining step as a change of control.

A change of control in certain heterogeneous reactions would be advantageous for the purpose of determining chemical rate constants k_c of surface reactions. Thus a change of control from the region of transport control to that of chemical control would make it possible for one to determine chemical rate constants directly. A change of control from the transport region to the region of intermediate kinetics might also suffice for a determination of k_c, because the use of equation (13), Section III(b) might yield a sufficiently accurate value for k_c. Consequently it is of importance to consider factors which might cause a shift of control towards or into the region of chemical control.

Any factor which causes an increase in the unit rate constant k_T of the transport process causes a shift of control towards the region of chemical control. In general, one way of increasing the value of k_T is by increasing the speed of rotation of a mechanical stirrer used to stir the reactive solution. The fact that a relationship exists between the

rate of dissolution of a solid and the speed of rotation of the stirrer is always correctly considered to be a proof of the fact that the process is taking place in the diffusion regime. At high speeds of rotation this relationship is generally less pronounced; however, this by no means proves a transition into the kinetic regime. Thus N.Y. Buben and D.A. Frank-Kamenetskü[52] have shown that this phenomenon can take place when a reaction is still completely controlled by convective-diffusive processes because, at high speeds of revolution, the paddle-type stirrer ceases to entrain liquid with it (they call this the "Slip Effect"). Clearly in order to decide in any given case whether the attainment of a limiting value for the observed rate constant is due to the stirrer having reached maximum efficiency, or whether there has been a change to chemical control, one must use other criteria. For example, baffles can be used with a view to promoting turbulence, so increasing the efficiency of the stirrer. If the observed rate constant then shows a definite increase, one can conclude that the reaction must still have been in the diffusion regime when the original limiting value was reached.

Another possible method of increasing the value of k_T would be to direct ultrasonic waves of sufficient energy on to the solid-liquid interface. If, as some workers have suggested (see the discussion in the Introduction), the effect of the ultrasonic waves is simply to decrease the thickness of the diffusion layer at the interface, then it is easy to see from the equation $k_T = \frac{D}{\delta}$ that the value of k_T must increase, with the consequence that there must be a shift towards chemical control. We have already mentioned the fact that some investigators have even suggested that ultrasonic waves can, in some cases at least, completely remove the diffusion layer from the interface. In such cases the heterogeneous reactions would be subject to chemical control.

A third means of effecting a shift of control towards the kinetic regime is by increasing the initial concentration of reactant. Reference to equation (7), Section III(b), i.e. $j = \frac{D(C - C_s)}{\delta}$, shows that the mass flux to the solid surface depends upon D, δ and the concentration difference $(C - C_s)$ at the interface. As δ is independent of the concentration difference at the interface and D is only slightly dependent on the concentration, it follows that a sufficiently large increase in the initial concentration of solute for a transport controlled reaction may increase j to such a point that the reaction at the surface can barely cope with the supply of reactive solute molecules or ions. Consequently with $C_s = C$, the convective-diffusive layer would disappear. An example of this effect is provided by the work of G.E. Boyd, A.W. Adamson and L.S. Myers[53] on the exchange adsorption of cations from aqueous solutions by phenol-formaldehyde resins: the observed rate is determined for 0.001 M-solutions by the rate at which cations are transported to the surface of the resin, whereas for 0.1 M-solution the observed rate is determined by the rate of cationic diffusion through the resin.

In some favourable cases, a change of temperature can be used to effect a change of control from one regime to another. A.C. Riddiford[54] has given a detailed treatment of the temperature coefficient of heterogeneous reactions and the following account is essentially based on his arguments.

The unit rate constants k_c and k_T, respectively, are assumed to be related to the absolute temperature Θ by means of the Arrhenius equations

$$k_c = Z_c e^{-E_c/R\Theta} \qquad \ldots\ldots (1)$$

and $$k_T = Z_T e^{-E_T/R\Theta} \qquad \ldots\ldots (2)$$

where E_c is the apparent critical increment (cf. Hinshelwood[55]) for the chemical process on the solid surface, E_T the activation energy for the

transport process, Z_c and Z_T the pre-exponential factors, and R the gas constant per gram molecule. θ is used in place of T in these equations to avoid confusion with the subscript denoting transport. Z_c is of the order of magnitude of the collision frequency per unit area of the solute molecules colliding with the solid surface, while Bircumshaw and Riddiford[56] have shown that Z_T is of the order of 100 or less. Consequently $Z_c \gg Z_T$. On the simple Nernst theory, E_T may be set equal to E_D, the energy of activation for diffusion, but this conclusion is based on the assumption that δ, the thickness of the Nernst diffusion layer, is temperature invariant. However, Riddiford[54] has shown that in general δ varies exponentially with temperature, but that the dependence is slight in comparison with the variation of the other quantities. He has also shown that E_T is somewhat smaller than E_D for laminar or mildly turbulent flow, whereas E_T may be large than E_D for strongly turbulent flow. As a rough rule, $E_T \doteqdot E_D$ when $a = \frac{2}{3}$, where a is the exponent in the general equation

$$\delta = \text{constant.}\ U^{-a}\, \nu^{(a-b)}\, D^{b} \qquad \ldots\ldots \quad (3)$$

equation (13) in the Introduction being a particular case of this equation. It has been found in practice that E_c varies from a lower limit of zero.

Combination of equations (21), Section III(b) and (1) and (2) of this Section, assuming that the pre-exponential factors and the activation energies are temperature invariant, leads to the equation

$$\frac{d(\ln k_1)}{d\theta} = \frac{1}{R\theta^2}\left[\left(\frac{k_c}{k_c + k_T}\right)E_T + \left(\frac{k_T}{k_c + k_T}\right)E_c\right] \qquad \ldots\ldots \quad (4)$$

If now an experimental energy of activation, E_A, be defined by the relationship $\frac{d(\ln k_1)}{d\theta} = \frac{E_A}{R\theta^2}$, then E_A can be determined at any value of θ from the corresponding tangent to the curve of $\ln k_1$ versus $1/\theta$.

A glance at equation (4) will show that

$$E_A = \left(\frac{k_c/k_T}{1 + k_c/k_T}\right) E_T + \left(\frac{1}{1 + k_c/k_T}\right) E_C \qquad \ldots\ldots \quad (5)$$

which shows that the variation of E_A with temperature depends upon the variation of the ratio k_c/k_T. Dividing equation (1) by (2) we have

$$k_c/k_T = \frac{Z_c}{Z_T} \cdot e^{(E_T - E_c)/P\theta} \qquad \ldots\ldots \quad (6)$$

Now $Z_c \gg Z_T$, so we may distinguish three cases:-

(i) when $E_c < E_T$, the term $e^{(E_T - E_c)/R\theta}$ in equation (6) is always positive and ranges in value from unity when $\theta \longrightarrow \infty$, to ∞ when $\theta \longrightarrow 0$, with the consequence that $k_c \gg k_T$, and $E_A = E_T$ at all temperatures;

(ii) when $E_c = E_T$, then equation (5) shows that $E_A = E_c = E_T$ and equation (6) shows that $k_c/k_T = \frac{Z_c}{Z_T} \gg 1$, i.e. the reaction will be diffusion controlled;

(iii) a case of considerable interest, when $E_c > E_T$, at low temperatures the observed rate will be chemically-controlled, while at high temperatures the heterogeneous reaction will be transport controlled. This can be seen by writing equation (6) as,

$$\frac{k_c}{k_T} = \frac{Z_c}{Z_T} \cdot \frac{1}{e^{(E_c - E_T)/R\theta}} ,$$

for then $E_c - E_T$ will be positive. Now $\lim_{\theta \longrightarrow 0} \frac{k_c}{k_T} = 0$, therefore

$\lim_{\theta \to 0} E_A = E_c$ (by equation (5); also $\lim_{\theta \to \infty} \frac{k_c}{k_T} = \frac{Z_c}{Z_T} \gg 1$,

therefore $\lim_{\theta \to \infty} E_A = E_T$. Those heterogeneous reactions which conform to case (iii) will experience a shift of control when the temperature is altered and if a sufficiently wide temperature range is practicable, a change of control will be experienced. The latter circumstances will be

manifested by a change of slope in the Arrhenius plot of ln k_1 versus $1/\theta$. Such a change was observed by C.M. Tu, H. Davis and H.C. Hottel[57] in their study of the combination of carbon spheres about one inch in diameter in a flowing air stream. An example of a heterogeneous reaction between a solid and liquid solution apparently conforming to case (iii) is that between very pure iron and hydrochloric acid studied by M.B. Abramson and C.V. King[58].

The argument just given depends inter alia upon the general validity of equations (1) and (2). These are normally at least approximately true, but specific examples are known or can be envisaged in which they may not apply. Thus one mechanism by which protons are made available at any site is thought to be by concerted electron switches along chains of orientated hydrogen-bonded water molecules. There does not appear to be any reason to believe that the effective average length of these chains (and therefore the rate constant) alters exponentially with the temperature. In fact it is also known that the arrangement of these chains alters from a "quartz-like" structure to a "cristobalite" structure as the temperature changes.

To summarise, it can be said that a shift of control in heterogeneous reactions between solids and liquid solutions towards or into the regime of chemical control can be effected by the following means: (a) increasing the initial concentration of the reactive solute(s), (b) by the use of sufficiently powerful ultrasonic waves, (c) by increasing the speed of rotation of the solid cylinder or disc, and (d) by lowering the temperature.

III(b) The Problem of Determining Chemical Rate Constants of Heterogeneous Reactions between Solids and Liquids the Rates of which are wholly or partly Controlled by Transport Processes

We have already referred to Van Name and Hill's classification of heterogeneous reactions and pointed out that in reality there is no sharp distinction between the three possible types of system. In the following discussion of the problem of determining chemical rate constants of heterogeneous reactions, we shall adhere to Van Name and Hill's classification.

The General Case (Van Name and Hill's Class C)

In this case there is a concentration gradient extending from the solid surface for a short distance into the solution. The concentration of solute at the surface is not zero but assumes some value C_s. In the steady state the rate at which solute molecules (or ions) are consumed by chemical reaction at the surface of solid is equal to the rate at which solute molecules (ions) are supplied by convective diffusion to the surface.

Before we derive an expression for the chemical rate constant in the general case, an important point concerning true and apparent surface areas of solids needs to be discussed. In general the rate of a transport controlled process is proportional to the apparent surface area A, but for a chemically controlled process the rate is a function of the true surface area A*. For a disc one face of which is exposed to attack by a reagent the apparent area $A = \pi r^2$, where r is its radius. During the course of a reaction A usually changes so slowly that it may be regarded as constant, but A* may increase appreciably owing to progressive roughening of the surface. If, however, the degree of smoothness of the surface remains the same during the course of reaction, then A* may be regarded as more or less constant. For one reason or another, e.g. adsorption of certain molecular or ionic

species on the surface of the solid, only a fraction σ of the surface area A^* may be available to the reactive solute and in such a case the rate of the chemical process is proportional to σA^*.

Let the mass flux, i.e. the number of grams of solute flowing through an area of one square centimetre per second, within the diffusion layer and normal to the surface be denoted by j. Therefore by Fick's first law of diffusion,

$$j = D\left(\frac{\partial c}{\partial x}\right)_{x=0} \qquad \ldots\ldots (1)$$

where $\left(\frac{\partial c}{\partial x}\right)_{x=0}$ is the concentration gradient at the surface. Very near the surface transport is virtually by diffusion only.

Let the amount in grams of solute which reacts per square centimetre of free surface in one second be denoted by q. Then the total amount that reacts per second over an area A^* sq.cm. $= \sigma A^* q$. For a chemical reaction of kinetic order m with respect to the solute, we have

$$q = k_c c_s^m \qquad \ldots\ldots (2)$$

where k_c is the chemical rate constant per unit area at unit volume and c_s the concentration in grams per c.c. of solute at the solid surface. Under steady state conditions, we have

$$\sigma A^* q = jA \qquad \ldots\ldots (3)$$

Substituting for q from equation (2) in equation (3), we get

$$\sigma A^* k_c C_s^m = jA$$

$$\text{or} \quad k_c = \frac{jA}{\sigma A^* c_s^m} \qquad \ldots\ldots (4)$$

If C denotes the concentration in the bulk of the solution, then for a linear concentration gradient (the Nernst case)

$$c = c_s + \left(\frac{\partial C}{\partial x}\right) \cdot \delta \qquad \ldots\ldots (5)$$

where δ = the thickness of the hypothetical Nernst layer.

$$\therefore \frac{\partial c}{\partial x} = \frac{c - c_s}{\delta} \qquad \ldots\ldots (6)$$

$\therefore$ Equation (1) becomes:

$$j = \frac{D(c - c_s)}{\delta} \qquad \ldots\ldots (7)$$

from which $c_s = c - \frac{j\delta}{D}$,

or $$c_s = c\left(1 - \frac{j\delta}{CD}\right) \qquad \ldots\ldots (8)$$

Substituting for C_s from equation (8) in equation (4), we get

$$k_c = \frac{jA}{\sigma A^* c^m \left(1 - \frac{j\delta}{CD}\right)^m}$$

or $$k_c = \frac{jA}{\sigma A^* \left(c - \frac{j\delta}{D}\right)^m} \qquad \ldots\ldots (9)$$

If $\sigma = 1$ and $A = A^*$, equation (9) reduces to

$$k_c = \frac{j}{\left(c - \frac{j\delta}{D}\right)^m} \qquad \ldots\ldots (10)$$

Knowing j for two different liquid velocities (different δ) at the same solute concentration c, we can determine the kinetic order m of the reaction from equation (9):

$$m \log_{10} \frac{\left(1 - \frac{j_1\delta_1}{cD}\right)}{\left(1 - \frac{j_2\delta_2}{cD}\right)} = \log_{10} \frac{j_1}{j_2}$$

$$\text{i.e., } m \log_{10}\left(\frac{cD - j_1\delta_1}{cD - j_2\delta_2}\right) = \log_{10} \frac{j_1}{j_2} \qquad \ldots\ldots (11)$$

Making use of equation (7) and equation (3) (in the Introduction), we note that

$$j = -\frac{V}{A}\left(\frac{dc}{dt}\right) \qquad \ldots\ldots (12)$$

Substituting for j from equation (12) in equation (9), we have

$$k_c = \frac{-V\left(\frac{dc}{dt}\right)}{\left[C + \frac{V\delta}{AD}\left(\frac{dc}{dt}\right)\right]^m \sigma A^*} \qquad \ldots\ldots (13)$$

Making the same substitution in equation (11), we have

$$m \log_{10}\left[\frac{CD + \frac{V\delta_1}{A}\left(\frac{dc}{dt}\right)_1}{CD + \frac{V\delta_2}{A}\left(\frac{dc}{dt}\right)_2}\right] = \log_{10}\frac{\left(\frac{dc}{dt}\right)_1}{\left(\frac{dc}{dt}\right)_2}$$

or

$$m \log_{10}\left[\frac{ACD + V\delta_1\left(\frac{dc}{dt}\right)_1}{ACD + V\delta_2\left(\frac{dc}{dt}\right)_2}\right] = \log_{10}\frac{\left(\frac{dc}{dt}\right)_1}{\left(\frac{dc}{dt}\right)_2} \qquad \ldots\ldots (14)$$

We can calculate k_c and m from equations (13) and (14) if we know the rates of reaction $\left(\frac{dc}{dt}\right)_1$ and $\left(\frac{dc}{dt}\right)_2$ for two different liquid velocities corresponding to two different thicknesses δ_1 and δ_2 of thr Nernst diffusion layer as well as, for k_c, values of σ and A^*. For a rotating disc under carefully controlled conditions[59] the thickness of the Nernst layer can be calculated from Levich's formula, $\delta = 1.61\, D^{\frac{1}{3}} \nu^{\frac{1}{6}} \omega^{-\frac{1}{2}}$ (equation (13) in the Introduction). The rates of reaction $\left(\frac{dc}{dt}\right)$ can easily be calculated from observations on the variation of the concentration C of solute with time.

It must be stressed that the above treatment is meant to apply to the steady state in the regime of intermediate kinetics when the chemical rate constant k_c is of comparable magnitude to the rate constant k_T of the transport process. When, however, the rate of the chemical reaction on the metal surface is so high that $C_s \longrightarrow 0$, the observed velocity constant per unit area at unit volume is equal to k_T, i.e. the overall

rate of the reaction is virtually transport controlled. This can most readily be seen by considering equations (3) and (4) in the Introduction, with k_T written for $\frac{D}{\delta}$:

$$-\frac{dc}{dt} = k_T \cdot \frac{A}{V}(C - C_s)$$

which reduces to $-\frac{dc}{dt} = k_T \cdot \frac{A}{V} \cdot \mathbf{c}$, when $\mathbf{c}_s = 0$, i.e., the observed first order rate constant per unit area at unit volume = k_T. Again when $\mathbf{c}_s \longrightarrow 0$, the difference between $\mathbf{c}$ and $j\delta/D$ becomes very small, so that a small error in the determination of j ($= -\frac{V}{A}\frac{dc}{dt}$) can lead to a large error in the determination of k_c by equations (9) or (10). Consequently values of k_c determined by this method for those reactions for which k_c is considerably greater than k_T are not very reliable.

We shall now derive a general expression for $-\frac{dc}{dt}$ in terms of k_c and k_T in the case of reactions in the intermediate regime. Substituting $-\frac{V}{A}(\frac{dc}{dt})$ for j in equation (4), we have $\sigma k_c A^* C_s^{\,m} = -\frac{V}{A}(\frac{dc}{dt}).A$,

$$\text{i.e., } -\frac{dc}{dt} = \sigma k_c \frac{A^*}{V} \mathbf{c}_s^{\,m} = -\frac{dC_s}{dt} \qquad \ldots\ldots (15)$$

But we know that $-\frac{dc}{dt} = k_T \cdot \frac{A}{V}(\mathbf{c} - \mathbf{c}_s)$.

$$\therefore \quad \frac{\sigma k_c A^*}{V} \cdot C_s^{\,m} = \frac{k_T A}{V}(\mathbf{c} - \mathbf{c}_s) \qquad \ldots\ldots (16)$$

Let us consider the simple case where the surface reaction is of the first order, i.e., where $m = 1$. Therefore from equation (16) we get

$$\mathbf{c}_s = \frac{k_T A \cdot \mathbf{c}}{\sigma k_c A^* + k_T A} \qquad \ldots\ldots (17)$$

Substituting for C_s from equation (17) in the equation

$$-\frac{dc}{dt} = k_T \cdot \frac{A}{V}(c - c_s), \text{ we get}$$

$$-\frac{dc}{dt} = k_T \cdot \frac{A}{V}\left(1 - \frac{k_T A}{\sigma k_c A^* + k_T A}\right) \cdot c$$

$$= \left(\frac{\sigma k_c k_T A^*}{k_T A + \sigma k_c A^*}\right) \cdot \frac{A}{V} \cdot c,$$

$$\text{i.e.} \quad -\frac{dc}{dt} = \left(\frac{k_c k_T}{\frac{k_T A}{\sigma A^*} + k_c}\right) \cdot \frac{A}{V} \cdot c \qquad \ldots\ldots \quad (18)$$

This equation tells us that for a heterogeneous reaction of intermediate type (Van Name and Hill's Class C) in the steady state the overall rate will follow a first order rate law provided A, A* and σ, or the product $A \cdot \frac{1}{\sigma A^*}$, remain constant during the course of the reaction. The observed rate constant per unit area at unit volume k_1 is then given by :

$$k_1 = k_c k_T \Big/ \left(\frac{k_T A}{\sigma A^*} + k_c\right) \qquad \ldots\ldots \quad (19)$$

If $\sigma = 1$ and $A^* = A$, equation (18) simplifies to,

$$-\frac{dc}{dt} = \left(\frac{k_c k_T}{k_T + k_c}\right) \cdot \frac{A}{V} \cdot c \qquad \ldots\ldots \quad (20)$$

and k_1 is then given by

$$k_1 = k_c k_T \Big/ (k_c + k_T) \qquad \ldots\ldots \quad (21)$$

If the kinetic order of the actual chemical reaction on the surface differs from unity, then the overall rate expressions are more complex than the simple first order expression of equation (20). Thus

Frank-Kammenetzkii[60] has shown that when m = 2, the overall expression for a reaction of intermediate type is given by

$$-\frac{dc}{dt} = k_T \cdot \frac{A}{V} \cdot \left[1 + \frac{k_T}{2k_c C} + \sqrt{\left(\frac{k_T}{k_c C} + \frac{k_T}{4k_c{}^2 C^2}\right)}\right] C$$

..... (22)

In some cases where it was not possible to calculate δ (or k_T) from the known properties of the system, it was nevertheless possible to determine k_c because k_T could be experimentally determined from observations on a series of similar chemical reactions which were taking place under such conditions that they were wholly transport controlled. For example, Hochberg and King[12] determined k_c for the reaction between a rotating cylinder of copper and the buffer system aqueous 0.1 M acetic acid/ 0.1 M sodium acetate in the presence of 3.5×10^{-3}M p-benzoquinone as depolarizer in a study of the dissolution of four metals, including copper, in acid solutions. In each case they used 250 ml. of solution at 25°C and a rate of revolution of 3,200 r.p.m. All the experiments were conducted under nitrogen. Their results are summarised in Table 48.

Table 48

Acid or buffer	Metal	k_1(cm./min.)
0.1 M - HCl, 0.05 M - glycine	Cadmium	0.88
0.03 M - HCl, 0.07 M - potassium hydrogen phthalate	Cadmium	0.82
0.1 M - acetic acid, 0.1 M sodium acetate	Cadmium	0.82
0.1 M - acetic acid, 0.1 M sodium acetate	Lead	0.86
0.1 M - HCl	Tin	0.86
0.1 M - acetic acid, 0.1 M sodium acetate	Copper	0.244

They obtained first order plots for all six reactions and the values of k_1 in cm/minute are recorded in the third column of the Table. The fact that the values of k_1 for the first five reactions are about the same suggests that they are all wholly transport controlled. Therefore $k_1 = k_T = 0.85$ cm/min. The fact that k_1 for copper is smaller than that for the other three metals suggests that the reaction involving copper may belong to the intermediate class and, as the observed reaction rate was strictly of the first order, Hochberg and King concluded that the chemical process at the metal surface was also first order, so that equation (21) could be used to calculate k_c:

$$0.244 = \frac{k_c \times 0.85}{k_c + 0.85} ,$$

$$\therefore k_c = 0.34 \text{ cm/min.}$$

They made no attempt to determine A* or σ, so it is not known whether the value 0.34 cm/min is that of the true chemical rate constant referred to unit area of actual surface.

When $k_c \ll k_T$, $C_s \longrightarrow C$. This can be seen by considering the general equation (16). The concentration gradient now virtually disappears. In this case the chemical reaction at the surface is so slow compared to the transport process that the reaction can barely cope with the supply of solute to the surface, with the result that the concentration of solute at the surface assumes the value of that in the bulk of the liquid. The overall rate is then chemically controlled and the observed velocity constant per unit area at unit volume is equal to k_c.

Roller's[9] Method of Determining Chemical Rate Constants of Heterogeneous Reactions

P. Roller considered the diffusion of solute within a prism of length L towards the surface of the reactive solid. The rate at which dissolved molecules disappear by reaction at the surface is equated to the

rate at which they diffuse from the neighbourhood of the surface to the surface, i.e.,

$$D \left(\frac{\partial c}{\partial x}\right)_{x = L} = - k_c C \qquad \ldots\ldots (23)$$

where D is the diffusion coefficient of the solute, k_c is the chemical rate constant per unit area of surface and $\left(\frac{\partial c}{\partial x}\right)_{x = L}$ is the concentration gradient at the surface. At the surface of the solution,

$$\left(\frac{\partial c}{\partial x}\right)_{x = 0} = 0 \qquad \ldots\ldots (24)$$

In the body of the solution the diffusion of solute is determined by the general diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad \ldots\ldots (25)$$

Equations (23) and (24) impose boundary conditions on the solution of equation (25). The initial condition is $C = C_o$ when $t = o$. Under these conditions, the solution of equation (25) is:

$$C = C_o \sum_1^{\infty} B_m e^{- \frac{D}{L^2} \beta_m^2 t} \cos \left(\frac{\beta_m}{L} x\right) \qquad \ldots\ldots (26)$$

where $\beta_m \tan \beta_m = \frac{k_c L}{D}$ $\qquad \ldots\ldots (27)$

and $B_m = \frac{4 \sin \beta_m}{2\beta_m + \sin 2\beta_m}$ $\qquad \ldots\ldots (28)$

Roller, in fact, states this solution without derivation. Since the solution is not immediately obvious, a method of deriving this result is given in an appendix on page 205.

The average concentration $\bar{C}$ throughout the solution is obtained by integration of equation (26) between the limits O and L, and dividing by L:

$$\bar{C} = \frac{1}{L}\int_0^L C_o \sum_1^{\infty} Bm \exp.\left(-\frac{D}{L^2}\beta_m{}^2 t\right)\cos\left(\frac{\beta_m}{L}\,x\right)dx\,,$$

$$\text{i.e.,}\quad \bar{C} = \bar{C}_o \sum_1^{\infty} \bar{B}_m\, e^{-\frac{D}{L^2}\beta_m{}^2 t} \qquad \ldots\ldots\ (29)$$

where β_m is as before given by equation (27), but $\bar{B}_m$ is now defined by

$$\bar{B}_m = \frac{4\sin^2\beta_m}{(2\beta_m + \sin 2\beta_m)\beta_m} \qquad \ldots\ldots\ (30)$$

Roller gives a numerical solution to equation (26) by drawing up a table which includes the first two terms $\bar{B}_1\, e^{-\frac{D}{L^2}B_1{}^2 t}$ and $\bar{B}_2\, e^{-\frac{D}{L^2}\beta_2{}^2 t}$ (also β_1 and β_2) for values of $\frac{k_c L}{D}$ from 0 to ∞, and for $\frac{Dt}{L^2}$ up to 1.6. The table shows that for an error < 1%, all terms but the first may be neglected provided $\frac{Dt}{L^2} \geqslant 0.2$. The table can be used to obtain the quantity $\frac{k_c L}{D}$. For L, one may substitute $\frac{V}{F}$, the ratio of the volume of the vessel to the surface area of the solid. In view of the fact that $\bar{C}$ is an average concentration, the same substitution appears feasible when the vessel is non-prismatic. Knowing the diffusion coefficient D and the depth of the vessel, k_c is readily obtained from the known value of $\frac{k_c L}{D}$.

The usual equation found for heterogeneous solid-liquid reactions is

$$\frac{d\bar{c}}{dt} = -k\frac{F}{V}\bar{c} \qquad \ldots\ldots\ (31)$$

where k is the observed rate constant.

The integrated from of this equation is:

$$k = -\frac{2.303}{t}\cdot\frac{V}{F}\cdot\log_{10}\frac{\bar{c}}{\bar{c}_o} \qquad \ldots\ldots\ (32)$$

Under the condition that all terms but the first may be neglected, i.e., for $\frac{Dt}{L^2} \geqslant 0.2$ for an error < 1%, equation (29) becomes

($\frac{V}{F}$ for L) : $$\log \frac{\bar{C}}{\bar{C}_o \bar{B}_1} = - \frac{F}{V} \cdot \frac{D}{L} \cdot \beta_1^2 t ,$$

$$\text{i.e.,} \quad \frac{D}{L} \beta_1^2 = - \frac{2.303}{t} \cdot \frac{V}{F} \cdot \log \frac{\bar{C}}{\bar{B}_1 \bar{C}_o} \qquad \ldots\ldots (33)$$

For values of $\frac{k_c L}{D} < 1$, which values are of most imterest, $\bar{B}_1$ in equation (33) is close to unity. with $\bar{B}_1$ assumed nearly equal to unity and $\frac{Dt}{L^2} \geqslant 0.2$, the right hand sides of equations (32) and (33) are substantially equal. Therefore

$$k = \frac{D}{L} \beta_1^2 \qquad \ldots\ldots (34)$$

Roller next obtains an explicit equation connecting k_c and the measured velocity constant per unit area at unit volume k. Referring to equation (27), it is seen that β_1^2 is a function of $\frac{k_c L}{D}$. Furthermore, β_1^2 must be zero for $\frac{k_c L}{D} = 0$, while β_1^2 must be finite for $\frac{k_c L}{D} = \infty$. In order to satisfy these requirements, Roller proposes the following function:

$$\beta_1^2 = \left(1 - e^{- \frac{k_c L}{D}}\right) \qquad \ldots\ldots (35)$$

Substitution of equation (35) in (34) gives:

$$k = \frac{D}{L} \left(1 - e^{- \frac{k_c L}{D}}\right) \qquad \ldots\ldots (36)$$

$$\therefore \quad e^{\frac{-k_c L}{D}} = 1 - \frac{kL}{D} ,$$

$$\text{i.e.,} \quad - \frac{k_c L}{D} = 2.303 \log_{10} \left(1 - \frac{kL}{D}\right),$$

$$\text{or} \quad k_c = - 2.303 \frac{D}{L} \log_{10} \left(1 - \frac{kL}{D}\right) \qquad \ldots\ldots (37)$$

The discussion of Roller's method so far has been restricted to systems in which the only transport process is diffusion of solute particles, i.e. in quiescent systems. However, as Roller himself points

out, modes of transport such as mechanical stirring, agitation etc., are much more effective than molecular diffusion in transferring solute particles from the bulk of the solution to the reactive solid surface. $\frac{D}{L}$ in equation (36) has the dimensions of velocity and it may be defined as the coefficient of transport by diffusion (compare this with the expression $k_T = \frac{D}{\delta}$, where δ is the thickness of the Nernst diffusion layer). An obvious extension of equation (36) is to replace the diffusion coefficient of transport, $\frac{D}{L}$, as simply a special case, by a general coefficient of transport, S. Equation (36) then becomes:

$$k = S\left(1 - e^{-\frac{k_c}{S}}\right) \qquad \ldots\ldots (38)$$

In order to express S in terms of measurable quantities, Roller appeals to the experimental results of various workers in the field of heterogeneous chemical reactions, notably Van Name and his co-workers. Making use of Van Name and Edgar's [4] result that rate constant varied with the 0.80 power of the stirring rate, he sets

$$S = Bs^{0.8} \qquad \ldots\ldots (39)$$

where s is the rate of stirring in r.p.m. and B is a constant which depends on the viscosity and density of the liquid. Substitution of this value for S in equation (38) gives:

$$k = Bs^{0.8}\left(1 - \exp\left[-k_c / Bs^{0.8}\right]\right) \qquad \ldots\ldots (40)$$

An exponent < 0.8 in equation (40) is due to the progressive influence of the chemical reaction velocity on the measured rate constant, while an exponent approaching unity might, according to Roller, obtain under exceptional conditions, e.g. a very high rate of stirring.

Equation (40) applies when transport is effected by mechanical stirring. To determine k_c, it is only necessary to evaluate B by measuring k at different stirring speeds. If the calculated value of k_c is to be accurate, its contribution to k must be sufficiently great. So k must be

measured at sufficiently high stirring speeds, and Roller gives the following criterion for deciding whether the range of speeds is proper to an accurate determination of k_c: if $\frac{k}{s^{0.8}}$ decreases sufficiently with increase in stirring speed, then the range of stirring speeds is suitable for an accurate determination of the unit rate constant k_c.

As examples to illustrate the application of the above criterion, Roller quotes several reactions from the chemical literature prior to 1935; we shall quote two of these examples (see the table). Clearly k_c cannot be determined accurately for the iodine-mercury reaction because the decrease in $k/s^{0.8}$ is < 2%; however the chemical rate constant can be calculated for the dissolution of zinc in 0.02 M copper sulphate solution because the decrease in $k/s^{0.8}$ is nearly 60%.

Table 49

Results Obtained at a Temperature of 25°C

Rate of oxidation of mercury by I_2 in KI solution, studied by Van Name and Edgar[4]			Rate of solution of Zn in 0.02 M $CuSO_4$ solution, studied by Centnerszwer and Heller[61]		
s in r.p.m.	k(observed)	$\left(k_{obs}/s^{0.8}\right) \times 10^3$	s in r.p.m.	k(observed)	$\left(k_{obs}/s^{0.8}\right) \times 10^3$
170	0.574	9.45	54	0.336	13.8
210	0.679	9.45	94	0.436	11.5
240	0.759	9.45	295	0.836	8.8
300	0.885	9.30	500	1.007	7.0
			600	1.061	6.4
			680	1.028	5.6

The Calculation of Chemical Rate Constants by the Use of Roller's Equation

Use is made of equation (40) of this section. In order to calculate k_c, the constant A must first of all be evaluated. As Roller gives no details of his method of calculating values of B, we suggest the following method.

The above mentioned equation can be rearranged to give,

$$1 - k/Bs^{0.8} = \exp\left[- k_c/Bs^{0.8}\right] \quad \ldots\ldots \quad (41)$$

Taking the logarithms of both sides of equation (1), we have

$$\log_e (1 - k/Bs^{0.8}) = - k_c/Bs^{0.8} \quad \ldots\ldots \quad (42)$$

If we determine the first order rate constants at two different stirring rates then, as both k_c and B are constant at a given temperature for a given solution, we have

$$\left.\begin{aligned} &\log_e (1 - k_1/Bs_1^{0.8}) = - k_c/Bs_1^{0.8} \\ \text{and} \quad &\log_e (1 - k_2/Bs_2^{0.8}) = - k_c/Bs_2^{0.8} \end{aligned}\right\} \quad \ldots\ldots \quad (43)$$

where k_1 and k_2 are, respectively, the first order rate constants measured at the corresponding speeds s_1 and s_2. Equation (43) gives

$$s_1^{0.8} \log_e (1 - k_1/Bs_1^{0.8}) = s_2^{0.8} \log_e (1 - k_2/Bs_2^{0.8}) \quad \ldots\ldots \quad (44)$$

$$\text{i.e.} \quad 1 - k_1/Bs_1^{0.8} = \left(1 - k_2/Bs_2^{0.8}\right)^{\left(\frac{s_2}{s_1}\right)^{0.8}} \quad \ldots\ldots \quad (45)$$

Next if in equation (45) we set $\dfrac{k_1}{s_1^{0.8}} = m_1$,

$$\frac{k_2}{s_2^{0.8}} = m_2,$$

and $\left(\dfrac{s_2}{s_1}\right)^{0.8} = R$, we get

$$1 - \frac{m_1}{B} = \left(1 - \frac{m_2}{B}\right)^R \quad , \text{i.e.,}$$

$$\left(1 - \frac{m_2}{B}\right)^R + \frac{m_1}{B} - 1 = 0 \quad \ldots\ldots \quad (46)$$

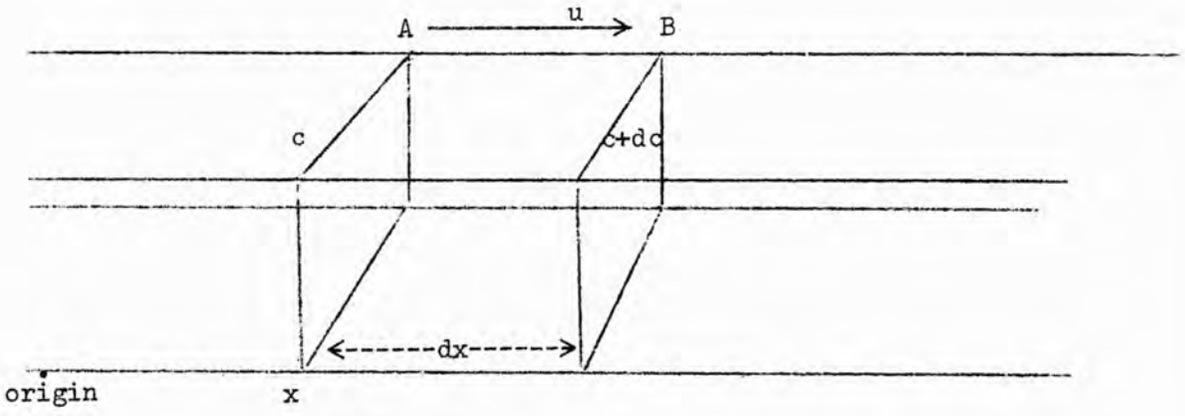
Now setting $\frac{1}{B} = x$ and $Z = 1 - m_2 x$, we have from equation (46),

$$Z^R + m_1\left(\frac{1 - Z}{m_2}\right) - 1 = 0,$$

i.e. $$Z^R - \frac{m_1}{m_2} \cdot Z + \frac{m_1}{m_2} - 1 = 0 \qquad \ldots\ldots \quad (47)$$

In general, the value of R will not be a simple integer. Equation (47) could be solved by numerical methods, but the method adopted here was to set R = 2 and, using our experimental results, to determine values of $\frac{n_1}{n_2}$ from a plot of values of $\log_{10} k$ against $\log_{10} s$. A concrete example illustrating the method is worked out in detail in Section II(m).

III(c) The General Equation for Convective-Diffusive Transport of Matter



Let c = the number of molecules per cubic centimetre at plane A.

O = the area of the end faces A and B of the rectangular cell shown.

D = the diffusion coefficient of the solute.

N = the total number of molecules.

u = the streaming velocity of the fluid in the positive direction.

Consider diffusion and convection along the x-coordinate only, and apply Fick's first law of diffusion to the diffusion of solute molecules from A to B, i.e., in the positive direction:

At A, $\frac{dN}{dt}$ = the total number of molecules flowing through A per second $= - DO\frac{\partial c}{\partial x}$ ..... (1)

$\therefore$ At B, $\frac{dN}{dt} = - DO\left\{\frac{\partial c}{\partial x} + \frac{\partial\left(\frac{\partial c}{\partial x}\right)}{\partial x} \cdot dx\right\}$

$= - DO\frac{\partial c}{\partial x} - DO\frac{\partial^2 c}{\partial x^2} \cdot dx$ ..... (2)

$\therefore$ Increase in the number of molecules in the cell per second

= Number entering per second at A - Number leaving per second through B

$= - DO\frac{\partial c}{\partial x} - \left\{- DO\frac{\partial c}{\partial x} - DO\frac{\partial^2 c}{\partial x^2} \cdot dx\right\}$

$= DO\frac{\partial^2 c}{\partial x^2} \cdot dx$

If we consider molecular diffusion alone, i.e. assume u = 0 the increase in concentration inside the cell per second $= \frac{\partial c}{\partial t}$ is given by

$$\frac{\partial c}{\partial t} = \frac{DO \frac{\partial^2 c}{\partial x^2} \cdot dx}{Odx},$$

i.e., $$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \ldots\ldots (3)$$

Equation (3) is the transport equation for the case of diffusion without convection. It has been solved for various boundary conditions, e.g., Roller[9] has found a solution for it in the case of diffusion in a prismatic vessel followed by chemical reaction.

Now consider the convection of the liquid medium from A to B.

Number of molecules passing A per second = Ouc ..... (4)

Number of molecules passing B per second = (c+dc)Ou ..... (5)

∴ Increase in the number of molecules in the cell per second = (4) - (5) = Ouc - (c + dc)Ou = - Oudc.

The total increase, i.e. due to both molecular diffusion and convection, in the number of molecules in the cell per second =

$$DO \frac{\partial^2 c}{\partial x^2} \cdot dx + (- Oudc) = DO \frac{\partial^2 c}{\partial x^2} \cdot dx - Oudc$$

∴ The increase in molecular concentration inside the cell per second $\left(= \frac{\partial c}{\partial t} \right)$ is given by

$$\frac{\partial c}{\partial t} = \frac{DO \frac{\partial^2 c}{\partial x^2} \cdot dx - Oudc}{Odx},$$

i.e. $$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} \quad \ldots\ldots (6)$$

Equation (6) is the general equation for the convective-diffusive transport of matter in the direction of the x-coordinate. The term $D \frac{\partial^2 c}{\partial x^2}$ is the contribution of molecular diffusion, while the term $U \frac{\partial c}{\partial x}$ is the contribution of convection to the total rate. In three

dimensions, the equation of convective-diffusive transport is

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) - \left(\frac{u\partial c}{\partial x} + \frac{v\partial c}{\partial y} + \frac{w\partial c}{\partial z}\right)$$

..... (7)

where u, v and w are respectively the components of the stream velocity of the liquid in the x, y and z directions. In many physicochemical kinetics experiments, solid discs or cylinders are made to rotate in liquid reagents such as aqueous acids, alkalis and halogens, and in order to be able to calculate the rate of mass transfer to the surfaces of these solids it is convenient to transform equation (7) into polar cylindrical coordinates. The result of the transformation is,

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{1}{r^2}\frac{\partial^2 c}{\partial \theta^2} + \frac{\partial^2 c}{\partial y^2}\right) - \left(v_r \frac{\partial c}{\partial r} + \frac{v_\theta}{r}\frac{\partial c}{\partial \theta} + v_y \frac{\partial c}{\partial y}\right)$$

..... (8)

The Application of the General Equation of Convective-Diffusive Transport of Matter to Physicochemical Problems

Before the general equation (8) can be solved for any practical system, expressions must be found for the fluid velocity components v_r, v_θ and v_y in terms of the appropriate coordinates of the system. This is done by solving the Navier-Stokes equations of fluid motion together with the equation of continuity. On the assumptions[62] that fluid flow is steady, that body forces can be neglected, and that all velocities and pressures within the fluid are independent of the angle θ and are functions of r and y only, the Navier-Stokes equations are expressed in cylindrical polar coordinates as follows:

$$v_r \frac{\partial v_r}{\partial r} - \frac{v_\theta^2}{r} + v_y \frac{\partial v_r}{\partial y} = -\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left(\frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r}\frac{\partial v_r}{\partial r} - \frac{v_r}{r^2} + \frac{\partial^2 v_r}{\partial y^2}\right)$$

..... (9)

$$v_r \frac{\partial v_\theta}{\partial r} + \frac{v_r v_\theta}{r} + v_y \frac{\partial v_\theta}{\partial y} = \nu\left(\frac{\partial^2 v_\theta}{\partial r^2} + \frac{1}{r}\frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r^2} + \frac{\partial^2 v_\theta}{\partial y^2}\right) \quad \ldots\ldots (10)$$

$$v_r \frac{\partial v_y}{\partial r} + v_y \frac{\partial v_y}{\partial y} = -\frac{1}{\rho}\frac{\partial p}{\partial y} + \nu\left(\frac{\partial^2 v_y}{\partial r^2} + \frac{1}{r}\frac{\partial v_y}{\partial r} + \frac{\partial^2 v_y}{\partial y^2}\right) \quad \ldots\ldots (11)$$

The equation of continuity is:

$$\frac{\partial v_r}{\partial r} + \frac{v_r}{r} + \frac{\partial v_y}{\partial y} = 0 \quad \ldots\ldots (12)$$

In these equations, p is the pressure in the liquid, ν the kinematic viscosity, and ρ is the density of the liquid, the other symbols having their usual significance.

We have already mentioned the fact that von Karman[33] solved equations (9) - (12) for the case of a large rotating disc in a large volume of liquid, and that Cochran[34] later improved von Karman's solution. In such a system we have $\frac{\partial p}{\partial r} = 0$, $\frac{\partial v_y}{\partial r} = 0$, $\frac{\partial^2 v_y}{\partial r^2} = 0$, so that the term $-\frac{1}{\rho}\frac{\partial p}{\partial r}$ vanishes from equation (9) while the terms $v_r \frac{\partial v_y}{\partial r}$, $\frac{\partial^2 v_y}{\partial r^2}$ and $\frac{1}{r}\frac{\partial v_y}{\partial r}$ all vanish from equation (11).

The methods adopted by von Karman and Cochran to solve these equations involve rather tedious series substitutions the details of which we shall not give here. Cochran's solution yields for v_y (which is the only velocity component needed in Levich's physicochemical treatment[29] of the rotating disc electrode) the value,

$$v_y = -(w\nu)^{\frac{1}{2}}\left[0.510\left(\frac{w}{\nu}\right)y^2 - 0.333\left(\frac{w}{\nu}\right)^{\frac{3}{2}}y^3 + 0.103\left(\frac{w}{\nu}\right)^2 y^4 \ldots\right] \quad \ldots\ldots (13)$$

Levich made simplifying assumptions which enabled him to reduce equation (8) to the much more simple equation, $D \frac{d^2c}{dy^2} = v_y \frac{dc}{dy}$. For v_y he substituted the right hand side of equation (13) and was thereby enabled to solve the problem of mass transport in laminar flow to a large rotating disc in a large volume of liquid, c.f. the Discussion and equations (11) to (14) in the Introduction .

In view of the fact that rotating cylinders have been much used in the study of heterogeneous reactions, it is interesting to investigate the solution of equation (8) in the case of two rotating concentric cylinders the annulus between which is filled with a viscous reactive fluid. Suppose the cylinders are both infinitely long thus reducing the problem to a plane one, and that both rotate about their common axis with different velocities. The Navier-Stokes equations can be considerably simplified because both v_r and v_y are zero, and, furthermore, $\frac{\partial v_\theta}{\partial y} = 0$, $\frac{\partial v_r}{\partial y} = 0$ and $\frac{\partial v_y}{\partial y} = 0$. Therefore we are left with

$$\frac{v_\theta^2}{r} = \frac{1}{\rho} \frac{dp}{dr} \qquad \ldots\ldots (14)$$

$$\frac{d^2 v_\theta}{dr^2} + \frac{1}{r} \frac{dv_\theta}{dr} - \frac{v_\theta}{r^2} = 0 \qquad \ldots\ldots (15)$$

Equation (15) has the general solution:

$$v_\theta = A r + \frac{B}{r} \qquad \ldots\ldots (16)$$

where A and B are constants for a given pair of cylinders rotating at given velocities. They can easily be determined with the aid of the boundary conditions $v_\theta = r_1 w_1$ at $r = r_1$ and $v_\theta = r_2 w_2$ at $r = r_2$, where r_1 and r_2 are respectively the radii of the inner and outer cylinder, and w_1 and w_2

are the respective angular velocities of the inner and outer cylinder. By substitution, we get

$$A = \frac{w_1 r_1^2 - w_2 r_2^2}{r_1^2 - r_2^2} \qquad \ldots\ldots (17)$$

$$B = \frac{(w_1 - w_2) r_1^2 r_2^2}{r_2^2 - r_1^2} \qquad \ldots\ldots (18)$$

In such an ideal system with laminar flow, the particles of liquid flow in concentric circles about the common axis with linear velocity v_θ depending on the radius r according to equation (16), and for a given r all the particles in the infinite cylindrical shell have the same v_θ because $\frac{\partial v_\theta}{\partial y} = 0$. There is no flow in the radial direction towards the cylinder walls.

In the special case of a single cylinder r_1 rotating in an infinite fluid, $r_2 \longrightarrow \infty$ and $w_2 = 0$. Hence A = 0 and equation (16) simplifies to:

$$v_\theta = \frac{w_1 r_1^2}{r} = \frac{\text{constant}}{r} \qquad \ldots\ldots (19)$$

Returning to the case of two concentric cylinders rotating about their common axis, we see that as there is no radial convection in the ideal case, transfer of reactive solute molecules to the cylinder surfaces must be by diffusion alone. The concentration c of solute is independent of both θ and y, so that all the first and second derivatives of c with respect to both θ and y in equation (8) are zero. Therefore, remembering also that $v_r = 0$, equation (8) reduces to:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) \qquad \ldots\ldots (20)$$

Now suppose the inner cylinder is made of magnesium and that it is rotating about its axis while the outer cylinder, which we may regard as

the unreactive wall of tbe containing vessel, is stationary. We may further suppose that the annular space between the cylinders is filled with a reactive solution such as hydrochloric acid. Our problem is to solve the partial differential equation (20) for c in terms of the time t and the radial distance r from the common axis of the cylinders, subject to the following initial and boundary conditions:

$c = c_o$ at $t = 0$ ..... Initial condition.

$\frac{\partial c}{\partial r} = 0$ at $r = b$, where b is the radius of the outer cylinder

$-D \frac{\partial c}{\partial r} = kc$ at $r = a$, where a is the radius of the inner cylinder

$a \leq r \leq b$ k is the chemical rate constant of the reaction between magnesium and acid, and D the diffusion coefficient of the acid.

} Boundary conditions

It will be noted that these initial and boundary conditions are similar to those of Roller[9] discussed earlier.

Let us assume a solution of the form

$$c = R(r).\ T(t) \qquad \ldots\ldots \quad (21)$$

where R(r) is a function of r only and T(t) is a function of t only. Therefore we have,

$$\frac{\partial c}{\partial t} = R(r).T'(t) \qquad \ldots\ldots \quad (22)$$

where T'(t) is the first partial derivative of T(t) with respect to t;

$$\frac{\partial c}{\partial r} = T(t).\ R'(r) \qquad \ldots\ldots \quad (23)$$

R'(r) being the first partial derivative of R(r) with respect to r;

$$\frac{\partial^2 c}{\partial r^2} = T(t).\ R''(r) \qquad \ldots\ldots \quad (24)$$

R''(r) being the second partial derivative of R(r) with respect to r. Now making the appropriate substitutions from (22), (23) in equation (20), we have,

$$\frac{1}{D} \cdot R(r) \cdot T'(t) = T(t) \cdot R''(r) + \frac{T(t) \cdot R'(r)}{r},$$

i.e., $$\frac{T'(t)}{D\,T(t)} = \frac{R''(r)}{R(r)} + \frac{R'(r)}{r} \qquad \ldots\ldots (25)$$

In equation (25) the variables are separate and in general we must set both sides of such an expression equal to a constant, say $\pm \lambda^2$. Using the negative sign before the constant, we have

$$\frac{T'(t)}{D\,T(t)} = -\lambda^2 = \frac{R''(r)}{R(r)} + \frac{R'(r)}{r\,R(r)},$$

hence $$T'(t) = -\lambda^2 D\,T(t) \qquad \ldots\ldots (26)$$

and $$r^2 R''(r) + r\,R'(r) + r^2 \lambda^2 R(r) = 0 \qquad \ldots\ldots (27)$$

We thus see that, using the method of the separation of variables, we have succeeded in arriving at two ordinary differential equations (26) and (27). Equation (26) is readily solved, giving

$$T(t) = X\, e^{-D\lambda^2 t} \qquad \ldots\ldots (28)$$

where X is a constant. Equation (27) is a form of Bessel's differential equation and its solution involves the use of infinite series known as Bessel functions. In our problem the range of r does not extend to the origin. Therefore in the general solution of equation (27), Bessel functions of the second kind of order zero must be used as well as those of the first kind. The general solution of this equation is,

$$R(r) = A\,J_o(\lambda r) + B\,Y_o(\lambda r) \qquad \ldots\ldots (29)$$

where $J_o(\lambda r)$ is a Bessel function of the first kind of zero order, $Y_o(\lambda r)$ is a Bessel function of the second kind of order zero, and A and B are arbitrary constants. Hence the solution of equation (20) is

$$c(r,t) = e^{-D\lambda^2 t}\left\{A\,J_o(\lambda r) + B\,Y_o(\lambda r)\right\} \qquad \ldots\ldots (30)$$

where, without loss of generality, X has been put equal to unity.

We must now apply our initial and boundary conditions to equation (30) in order to try to obtain an explicit solution to our problem. Making use of the following property of the Bessel functions, $\frac{\partial J_o(\lambda r)}{\partial r} = -\lambda J_1(\lambda r)$ $\frac{\partial Y_o(\lambda r)}{\partial r} = -\lambda Y_1(\lambda r)$, and applying the boundary condition $\frac{\partial c}{\partial r} = 0$ at $r = b$ to equation (30), we have

$$0 = -\lambda e^{-D\lambda^2 t}\left\{AJ_1(\lambda b) + B\,Y_1(\lambda b)\right\},$$

i.e., $$\frac{A}{B} = -\frac{Y_1(\lambda b)}{J_1(\lambda b)} \qquad \ldots\ldots (31)$$

Upon substituting for c and $\frac{\partial c}{\partial r}$ in the boundary condition equation $-D\frac{\partial c}{\partial r} = k\,c$ at $r = a$, we have

$$k[A\,J_o(\lambda a) + B\,Y_o(\lambda a)]e^{-D\lambda^2 t} = \lambda De^{-D\lambda^2 t}\left[A\,J_1(\lambda a) + B\,Y_1(\lambda a)\right]$$

i.e., $$\frac{k}{D} = \frac{\lambda[A\,J_1(\lambda a) + B\,Y_1(\lambda a)]}{[A\,J_o(\lambda a) + BY_o(\lambda a)]} \qquad \ldots\ldots (32)$$

If we substitute the value of A given by equation (31) in equation (32), we obtain

$$\frac{k}{D} = \frac{\lambda[J_1(\lambda b)\,Y_1(\lambda a) - J_1(\lambda a)\,Y_1(\lambda b)]}{[J_1(\lambda b)\,Y_o(\lambda a) - J_o(\lambda a)\,Y_1(\lambda b)]} \qquad \ldots\ldots (33)$$

The expression

$$A\left(J_o(\lambda r) - \frac{J_1(\lambda b)}{Y_1(\lambda b)} \cdot Y_o(\lambda r)\right)e^{-D\lambda^2 t}$$

satisfies equation (20) and the boundary conditions, where A is an arbitrary constant and λ is any root other than zero of equation (33).

The general solution of equation (20) is

$$c(r,t) = \sum_{n=1}^{\infty} A_n e^{-D\lambda_n^2 t}[J_o(\lambda_n r)\,Y_1(\lambda_n b) - J_1(\lambda_n b)\,Y_o(\lambda_n r)$$

$\ldots\ldots (34)$

The values of the constants A_n can be determined in the following way, making use of the initial condition that $c(r,t) = c_o$ at $t = 0$. Equation (34) then becomes

$$c_o = \sum_{n=1}^{\infty} A_n \cdot \phi_o(\lambda_n r) \qquad \ldots\ldots (35)$$

where we have written $\phi_o(\lambda_n r)$ for $[J_o(\lambda_n r)\, Y_1(\lambda_n b) - J_1(\lambda_n b) Y_o(\lambda_n r)]$. Multiplying both sides of equation (35) by $r\phi_o(\lambda_n r)$, we have

$$rc_o\phi_o(\lambda_n r) = rA_1\phi_o(\lambda_1 r)\phi_o(\lambda_n r) + rA_2\phi_o(\lambda_2 r)\phi_o(\lambda_n r) \ldots\ldots rA_n[\phi_o(\lambda_n r)]^2$$

$\ldots\ldots$ (36)

Integration of equation (36) between the limits a and b gives

$$c_o \int_a^b r\phi_o(\lambda_n r)dr = A_1 \int_a^b r\phi_o(\lambda_1 r)\phi_o(\lambda_n r)dr + \ldots\ldots A_n \int_a^b r[\phi_o(\lambda_n r)]^2 dr$$

$\ldots\ldots$ (37)

By a standard procedure[63] and using the first boundary condition $\phi_o^{\,1}(\lambda b) = 0$, we have

$$\int_a^b r\phi_o(\lambda_1 r)\phi_o(\lambda_2 r)dr = 0,$$

provided λ_1 and λ_2 are two distinct roots of

(i) $\phi_o(\lambda a) = 0$

or (ii) $\phi_o^{\,1}(\lambda a) = 0$

or (iii) $\lambda \phi_o^{\,1}(\lambda a) + h\phi_o(\lambda a) = 0,$

where $\phi_o^{\,1}(\lambda a) = \left(\frac{d\phi_o(x)}{dx}\right)_{x = \lambda a}$, and h is an arbitrary constant.

In our case, condition (iii) is satisfied because it is the same as the second boundary condition $\lambda \phi_o^{\,1}(\lambda a) = -\frac{k}{D}\phi_o(\lambda a)$. Therefore it follows

that all the integrals on the right hand side of equation (37) except the integral $\int_a^b r[\phi_o(\lambda_n r)]^2 dr$ vanish, so we are left with

$$c_o \int_a^b r\phi_o(\lambda_n r)dr = A_n \int_a^b r[\phi_o(\lambda_n r)]^2 dr,$$

from which

$$A_n = \frac{c_o \int_a^b r\phi_o(\lambda_n r)dr}{\int_a^b r[\phi_o(\lambda_n r)]^2 dr} \qquad \ldots\ldots \quad (38)$$

Substituting the value of A_n given by equation (38) in equation (34), we have

$$c(r,t) = c_o \sum_{n=1}^{\infty} \frac{e^{-D\lambda_n^2 t} \cdot \phi_o(\lambda_n r) \cdot \int_a^b r\phi_o(\lambda_n r)dr}{\int_a^b r[\phi_o(\lambda_n r)]^2 dr} \qquad \ldots\ldots \quad (39)$$

Equation (39) is the formal general solution of equation (20) subject to the initial and boundary conditions. With its aid we can calculate the variation of solute concentration with respect to radial distance r from the axis of the concentric cylinders and the time t, when the solution is in laminar flow.

It would be interesting to investigate whether it is at all possible to adapt the solution of equation (39) to a more practical situation, such as a cylinder rotating in a reaction vessel in the shape of a conical flask or a beaker, with the liquid in turbulent motion. If such a solution could be found, it might then be possible to develop a method of calculating values of k_c, the chemical rate constants, as an alternative to Roller's method.

Thanks are due to Dr. Bhagavan of the Mathematics Department, Bedford College for helpful discussion of the boundary conditions introduced above.

III(d) Rate Equations for Heterogeneous Reactions between Solids and Liquids when the Apparent Surface Area A of Solid varies Appreciably during the Course of Reaction

No theoretical treatment of rate equations for heterogeneous reactions in the case where the apparent area of a dissolving massive solid changes appreciably during the course of reaction seems to have appeared in the literature. We here present a treatment that specifically applies to rate equations in the case of magnesium cylinders dissolving in acid solutions.

Let us consider the reaction between the curved surface of a magnesium cylinder of radius r cm. and an acid solution of volume V c.c. In time dt seconds let the decrease in concentration of the acid be dc grams per c.c.

$\therefore$. The number of grams that have disappeared from the volume V = Vdc.

$\therefore$. The number of grams (m) of magnesium that have disappeared = $\frac{12.16\ Vdc}{E}$, where E is the equivalent weight in grams of the acid.

Now $\rho = \frac{m}{v}$, where ρ = the density of the solid, m its mass and v its volume.

In this case, $m = \frac{12.16\ Vdc}{E}$,

$v = 2\pi rhdr$, where h = the length of the cylinder and dr = the decrease in its radius in time dt sec.

$$\therefore\ \rho = \frac{12.16\ Vdc}{2\pi rhEdr} = \frac{6.08\ Vdc}{\pi rhEdr}$$

so $$dc = \frac{\pi rh\rho E}{6.08\ V} \cdot dr \qquad \ldots\ldots\ (1)$$

Integration of equation (1) gives:

$$c = \frac{\pi h\rho E r^2}{12.16\ V} + I \qquad \ldots\ldots\ (2)$$

where I is a constant of integration.

Many heterogeneous reactions between various solids and different liquids have been investigated kinetically[64] and it has been found that they obey rate equations of the following form:

$$-\frac{dc}{dt} = \frac{k\,A}{V} \cdot c^n \qquad \ldots\ldots (3),$$

where k = the rate constant per unit area at unit volume, A = the area of solid exposed to attack by the liquid reagent, V = the volume of the liquid. In most of these investigations, the area A has been assumed to be constant during the course of reaction. It has been found in many cases that the exponent n is unity, i.e., the reaction is of the first order in reagent concentration c. Substituting the value of dc given by equation (1) in equation (3), we have:

$$-\frac{\pi r h \rho E}{6.08\,V} \cdot \frac{dr}{dt} = k \cdot \frac{2\pi r h}{V} \cdot c^n,$$

$$\text{i.e.,}\quad -\frac{dr}{dt} = \frac{12.16\,k}{\rho E} \cdot c^n \qquad \ldots\ldots (4)$$

If the reaction is of the first order, n = 1 and equation (4) becomes:

$$-\frac{dr}{dt} = \frac{12.16\,k}{\rho E} \cdot c \qquad \ldots\ldots (5)$$

Substituting the value of c given by equation (2) in equation (5), we have:

$$-\frac{dr}{dt} = \frac{12.16\,k}{\rho E}\left(\frac{\pi h \rho E r^2}{12.16\,V} + I\right)$$

$$= \frac{\pi k h}{V}(r^2 + a^2), \quad \text{where } a^2 = \frac{12.16\,VI}{\pi h \rho E}$$

$$\text{so}\quad -\frac{dr}{(r^2 + a^2)} = \frac{\pi k h}{V} \cdot dt \qquad \ldots\ldots (6)$$

Integration of equation (6) gives:

$$-\frac{1}{a}\,\mathrm{Tan}^{-1}\left(\frac{r}{a}\right) = \frac{\pi k h}{V} \cdot t + I',$$

i.e., $$\mathrm{Tan}^{-1}\left(\frac{r}{a}\right) = -\left(\frac{\pi k h a}{V}\right) \cdot t + I'' \qquad \ldots\ldots\ldots (7),$$

where I'' is a constant of integration. Thus if the reaction between the metal cylinder and the acid is of the first order, a plot of $\mathrm{Tan}^{-1}\left(\frac{r}{a}\right)$ versus time should give a straight line with a negative slope. This slope is numerically equal to $\frac{\pi k h a}{V}$, so that if we denote the slope by m we can calculate the rate constant k from the relationship

$$k = \frac{mV}{\pi h a} \qquad \ldots\ldots (8)$$

Here $a = \sqrt{\frac{12.16\ VI}{\pi h \rho E}}$, and it can be seen from equation (2) that $I = c_t$ the concentration of the acid when r = 0, i.e. when all of the magnesium has dissolved; this can easily be calculated from the known amount of magnesium and the initial concentration and volume of the acid.

The rate constant k can also be calculated by a non-graphical method, for it can be seen from equation (7) that

$$k = \frac{(\theta_1 - \theta_2)V}{\pi h t a} \qquad \ldots\ldots (9),$$

where $\theta_1 = \mathrm{Tan}^{-1}\left(\frac{r_1}{a}\right)$, $\theta_2 = \mathrm{Tan}^{-1}\left(\frac{r_2}{a}\right)$, r_1 and r_2 the radius of the cylinder at times t_1 and t_2, respectively, after the commencement of the reaction, and $t = t_2 - t_1$.

If we refer again to equation (4) and put n = 2, i.e. the reaction between metal and solution is of the second order, we have:

$$-\frac{dr}{dt} = \frac{12.16\ k}{\rho E} \cdot c^2 \qquad \ldots\ldots (10)$$

Substituting the value of c given by equation (2) in equation (10), we have

$$-\frac{dr}{dt} = \frac{12.16\ k}{\rho E}\left\{\frac{\pi h\rho E r^2}{12.16\ V} + I\right\}^2$$

$$= \frac{12.16\ k}{\rho E}\left(\frac{\pi h\rho E}{12.16\ V}\right)^2\left\{r^2 + \frac{12.16\ VI}{\pi h\rho E}\right\}^2$$

$$= \frac{k\rho E\pi^2 h^2}{12.16\ V^2}\left\{r^2 + \frac{12.16\ VI}{\pi h\rho E}\right\}^2$$

$$= \frac{k\rho E\pi^2 h^2}{12.16\ V^2}\left\{r^2 + a^2\right\}^2, \text{ where, as before}$$

$a^2 = \frac{12.16\ VI}{\pi h\rho E}$, so, after separation of variables, we have

$$\frac{-dr}{(r^2+a^2)^2} = \frac{k\rho E\pi^2 h^2}{12.16\ V^2}\cdot dt \qquad \ldots\ldots \quad (11)$$

The left hand side of equation (11) can be integrated by making use of the following reduction formula:

$$\frac{x}{(x^2+a^2)^m} = 2ma^2 J_{m+1} - (2m-1)J_m ,$$

where $J_m(x) = \int \frac{dx}{(x^2+a^2)^m}$. In our case, m = 1, so we have:

$$\int \frac{dr}{(r^2+a^2)^2} = \frac{r}{2(r^2+a^2)a^2} + \frac{1}{2a^3}\,\mathrm{Tan}^{-1}\left(\frac{r}{a}\right).$$

On integrating both sides of equation (11), there results:

$$\frac{r}{2a^2(r^2+a^2)} + \frac{1}{2a^3}\,\mathrm{Tan}^{-1}\left(\frac{r}{a}\right) = -\frac{k\rho E\pi^2 h^2 t}{12.16\ V^2} + I''' \quad \ldots\ldots$$

i.e., $$\frac{ar}{(r^2+a^2)} + \mathrm{Tan}^{-1}\left(\frac{r}{a}\right) = -\frac{k\rho E\pi^2 h^2 a^3 t}{6.08\ V^2} + I'''$$

$\ldots\ldots$ (12)

where I''' is an integration constant.

If the reaction between the magnesium and acid is of the second order, a plot of $\left\{ar(r^2 + a^2)^{-1} + \mathrm{Tan}^{-1}\left(\frac{r}{a}\right)\right\}$ versus time should give a straight line with a negative slope. This slope should numerically be equal to $\frac{k\rho E\pi^2 h^2 a^3}{6.08\ V^2}$, so we can calculate the rate constant from the relationship

$$k = \frac{6.08\ V^2 m}{\rho E\pi^2 h^2 a^3} \qquad \ldots\ldots \quad (13)$$

where m is the numerical value of the slope. The constant k can be calculated by a non-graphical method, for we can see from equation (12) that

$$k_2 = \frac{6.08\ V^2 \left[a\left\{\frac{r_1}{r_1^2 + a^2} - \frac{r_2}{r_2^2 + a^2}\right\} + \theta_1 - \theta_2\right]}{\rho E\pi^2 h^2 a^3 (t_2 - t_1)} \qquad \ldots\ldots \quad (14)$$

where $\theta_1 = \mathrm{Tan}^{-1}\left(\frac{r_1}{a}\right)$, $\theta_2 = \mathrm{Tan}^{-1}\left(\frac{r_2}{a}\right)$, r_1 and r_2 being successive values of the cylinder radius.

The integral $\int \frac{dr}{(r^2 + a^2)^3}$, which is required to work out the rate expression for a third order reaction, can also be evaluated by using the same reduction formula as we have just used in working out the second order rate expression. Thus we have,

$$\int \frac{dr}{(r^2 + a^2)^3} = \frac{r}{4a^2(r^2 + a^2)^2} + \frac{3r}{8a^4(r^2 + a^2)} + \frac{3}{8a^5}\mathrm{Tan}^{-1}\left(\frac{r}{a}\right)$$

In Table 50 are collected the integrated rate expressions in the case of reactions between magnesium and acids when the order of reaction n is given values of 1, $\frac{3}{2}$, 2 and 3, respectively.

Table 50

Order of reaction between magnesium and acid	Integrated Rate Expression
1	$\mathrm{Tan}^{-1}\left(\frac{r}{a}\right) = -\frac{\pi h a k}{V} \cdot t + I'$
$\frac{3}{2}$	$\frac{r}{a^2(r^2+a^2)^{\frac{1}{2}}} = -\frac{k(\pi h)^{3/2}(\rho E)^{\frac{1}{2}}}{(12.16)^{\frac{1}{2}} V^{3/2}} \cdot t + I''$
2	$\frac{ar}{r^2+a^2} + \mathrm{Tan}^{-1}\left(\frac{r}{a}\right) = -\frac{\rho E \pi^2 h^2 a^3 k}{6.08\, V^2} \cdot t + I'''$
3	$\frac{2a^3 r}{3(r^2+a^2)^2} + \frac{ar}{(r^2+a^2)} + \mathrm{Tan}^{-1}\left(\frac{r}{a}\right) = -\frac{8E^2 d^2 \pi^3 h^3 a^5 k}{3(12.16)^2 V^3} \cdot t + I''''$

In Table 51 are collected expressions for the rate constants k (with subscripts indicating the value of n), calculated by a non-graphical method from the expressions in Table 50. The significance of the symbols θ_1, θ_2, θ, θ_s, r and r_s in Table 51 are as follows:-
$\theta_1 = \mathrm{Tan}^{-1}\left(\frac{r_1}{a}\right)$, $\theta_2 = \mathrm{Tan}^{-1}\left(\frac{r_2}{a}\right)$, θ is the value of $\mathrm{Tan}^{-1}\left(\frac{r}{a}\right)$ at the beginning of the reaction when the cylinder radius is r, and θ_s the value of $\mathrm{Tan}^{-1}\left(\frac{r}{a}\right)$ at time t from the beginning of the reaction when the radius of the cylinder is r_s.

The above treatment of the heterogeneous reaction between magnesium and acids assumes that the specific rate constant k is independent of the diameter of the metal cylinder. However, it appears from the work of Eisenberg, Tobias and Wilke[32] that, for reactions the rates of which are controlled by transport processes, k may well be proportional to the cylinder diameter d_i raised to the power of 0.4. These investigators studied the dissolution of cylinders of benzoic and cinnamic acids in aqueous glycerol solutions, also the electrolytic oxidation-reduction reaction between potassium ferrocyanide and potassium ferricyanide in aqueous alkali solutions at the curved surface of nickel cylinders rotating about their axes in the centre of static, circular, cylindrical electrodes of the same material, the aqueous solution filling the annular space between the electrodes.

Eisenberg, Tobias and Wilke found that in the Reynold's Number range of 1,000 - 100,000 their data can best be represented by the following equation:

$$\frac{k}{P}(Sc)^{0.644} = 0.0791\,(Rd)^{-0.3} \qquad \ldots\ldots \quad (15)$$

where k is the rate constant per unit area at unit volume for the reaction (or dissolution process) in cm/sec., P (the authors use V) the peripheral velocity of the cylinder in cm/sec., Sc the Schmidt Number, and Rd the Reynold's Number.

Table 51

The Rate Constant Expressions for Different Orders of Reaction Between Magnesium and Acid

Order	Expression
1	$k_1 = \dfrac{(\theta_1 - \theta_2)V}{\pi h a (t_2 - t_1)}$
	OR $k_1 = \dfrac{(\theta - \theta_s)V}{\pi h a t}$
$\frac{3}{2}$	$k_{\frac{3}{2}} = \dfrac{(12.16)^{\frac{1}{2}} V^{\frac{3}{2}} \left\{ \dfrac{r_1}{(r_1^2 + a^2)^{\frac{1}{2}}} - \dfrac{r_2}{(r_2^2 + a^2)^{\frac{1}{2}}} \right\}}{(\rho E)^{\frac{1}{2}} (\pi h)^{3/2} a^2 (t_2 - t_1)}$
	OR $k_{\frac{3}{2}} = \dfrac{(12.16)^{\frac{1}{2}} V^{\frac{3}{2}} \left\{ \dfrac{r}{(r^2 + a^2)^{\frac{1}{2}}} - \dfrac{r_s}{(r_s^2 + a^2)^{\frac{1}{2}}} \right\}}{(\rho E)^{\frac{1}{2}} (\pi h)^{3/2} a^2 t}$
2	$k_2 = \dfrac{6.08 V^2 \left[a \left\{ \dfrac{r_1}{r_1^2 + a^2} - \dfrac{r_2}{r_2^2 + a^2} \right\} + \theta_1 - \theta_2 \right]}{\rho E \pi^2 h^2 a^3 (t_2 - t_1)}$
	OR $k_2 = \dfrac{6.08 V^2 \left[a \left\{ \dfrac{r}{r^2 + a^2} - \dfrac{r_s}{r_s^2 + a^2} \right\} + \theta - \theta_s \right]}{\rho E \pi^2 h^2 a^3 t}$
3	$k_3 = \dfrac{3(12.16)^2 V^3 \left[\dfrac{2a^3}{3} \left\{ \dfrac{r_1}{(r_1^2 + a^2)^2} - \dfrac{r_2}{(r_2^2 + a^2)^2} \right\} + a \left\{ \dfrac{r_1}{r_1^2 + a^2} - \dfrac{r_2}{r_1^2 + a^2} \right\} + \theta_1 - \theta_2 \right]}{8 \rho^2 E^2 \pi^3 h^3 a^5 (t_2 - t_1)}$
	OR $k_3 = \dfrac{3(12.16)^2 V^3 \left[\dfrac{2a^3}{3} \left\{ \dfrac{r}{(r^2 + a^2)^2} - \dfrac{r_s}{(r_s^2 + a^2)^2} \right\} + a \left\{ \dfrac{r}{r^2 + a^2} - \dfrac{r_s}{r_s^2 + a^2} \right\} + \theta - \theta_s \right]}{8 \rho^2 E^2 \pi^3 h^3 a^5 t}$

$Rd = \frac{Pd_i}{\nu}$, where d_i = cylinder diameter in cm., and

ν = kinematic viscosity in cm^2/sec.

$Sc = \frac{\mu}{\rho D}$ where μ = viscosity of the solution in c.g.s. units,

ρ = its density in gm/c.c., and D = the coefficient of

$= \frac{\nu}{D}$ diffusion of the reactive solute in cm^2/sec

By making use of the definitions of the Reynold and Schmidt Numbers just given, we can cast equation (15) into the following form:

$$k = 0.0791\ P \left(\frac{Pd_i}{\nu}\right)^{-0.3} \left(\frac{\nu}{D}\right)^{-0.644}$$

$$= 0.0791\ \pi^{0.7}\ S^{0.7} d_i^{0.4}\ \nu^{-0.344}\ D^{0.644} \qquad \ldots\ldots\ (16)$$

where S = the rotational speed of the cylinder in revolutions per second (r.p.s.). This equation (16) shows us that Eisenberg, Tobias and Wilke succeeded in incoporating into a single correlation the effect of cylinder diameter, speed of rotation, diffusion coefficient and viscosity on mass transfer rates. It is interesting to note that Roald and Beck[49] found a relationship of the form k = constant. $P^{0.7}$ for magnesium cylinder electrodes rotating in hydrochloric acid. This relationship follows from equation (16), for a given system (constant ν and D) and rotor diameter. Furthermore Brunner's[2] results, represented by the equation k = constant $S^{\frac{2}{3}}$, for a given rotor diameter and a given set of physical properties of the system, are in approximate agreement with equation (16). On the other hand, a linear dependence of dissolution rates or limiting currents on the velocity of rotation proposed by King and Schack[21], is not in agreement with equation (16).

Provided that equation (16) can be applied to the dissolution of magnesium cylinders in acids under the conditions obtaining in our experiments, we must modify our rate equation (4) to allow for the fact that the rate constant k depends upon the cylinder diameter. For a given set of physical properties (constant ν and D) and a constant speed of rotation S, equation (16) reduces to:

$$k = \kappa r^{0.4} \qquad \ldots\ldots (17)$$

where $\kappa = 0.0791\ \pi^{0.7}\ S^{0.7}\ \nu^{-0.344}\ D^{0.644}\ .2^{0.4}$ is a constant at a given temperature. Substitution of (17) in (4) gives:

$$-\frac{dr}{dt} = \frac{12.16\ \kappa\ r^{0.4}}{\rho E} \cdot C^n \qquad \ldots\ldots (18)$$

Substituting the value of C given by equation (2) in equation (18) and putting n = 1, we get:

$$-\frac{dr}{r^{0.4}\ (r^2 + a^2)} = \frac{\pi\kappa h}{V} \cdot dt \qquad \ldots\ldots (19)$$

If the reaction between magnesium and acid is of the second order, i.e., n = 2, equation (18) becomes:

$$-\frac{dr}{r^{0.4}(r^2 + a^2)^2} = \frac{\kappa\rho E\pi^2 h^2}{12.16\ V^2} \cdot dt \qquad \ldots\ldots (20)$$

Integration of equations (19) and (20) between the limits, r_1 at time t_1, and r_2 at a later time t_2 ($r_1 > r_2$) gives:

$$-\int_{r_1}^{r_2} \frac{dr}{r^{0.4}(r^2 + a^2)} = \frac{\pi\kappa h}{V} \cdot t \qquad \ldots\ldots (21)$$

and $$-\int_{r_1}^{r_2} \frac{dr}{r^{0.4}(r^2 + a^2)^2} = \frac{\kappa\rho E\pi^2 h^2}{12.16\ V^2} \cdot t \qquad \ldots\ldots (22)$$

where $t = t_2 - t_1$. The integrals $\int_{r_1}^{r_2} \frac{dr}{r^{0.4}(r^2 + a^2)}$ and $\int_{r_1}^{r_2} \frac{dr}{r^{0.4}(r^2 + a^2)^2}$ can be evaluated by numerical methods, e.g., by using Simpson's rule.

There are two methods that can be used to determine the order of reaction in such cases as we have just been discussing:

(a) The Method of Integration;

(b) The Differential Method.

We shall discuss each of these methods in tunr.

(a) The Method of Integration

For our purpose we write equations (21) and (22), respectively, in the following forms:

$$\int_{r_2}^{r_1} \frac{dr}{r^{0.4}(r^2 + a^2)} = X_1 t, \text{ where } X_1 = \frac{\pi h \kappa}{V}, \text{ a constant,}$$

$$\text{or } X_1 = \frac{1}{t} \int_{r_2}^{r_1} \frac{dr}{r^{0.4}(r^2 + a^2)} \quad \text{for a first order reaction;}$$

$$\int_{r_2}^{r_1} \frac{dr}{r^{0.4}(r^2 + a^2)^2} = X_2 t, \text{ where } X_2 = \frac{\kappa \rho E \pi^2 h^2}{12.16\, V^2}, \text{ a constant}$$

$$\text{or } X_2 = \frac{1}{t} \int_{r_2}^{r_1} \frac{dr}{r^{0.4}(r^2 + a^2)^2} \quad \text{for a second order reaction.}$$

In general, for an n^{th} order reaction, we have

$$X_n = \frac{1}{t} \int_{r_2}^{r_1} \frac{dr}{r^{0.4}(r^2 + a^2)^n} \qquad \ldots\ldots (23)$$

The procedure to be adopted is to determine the radius of a given cylinder rotating in acid solution after various intervas of time, and to substitute the data in these equations. The equation corresponding most closely to the correct order of the reaction should give the most constant value of X.

(b) The Differential Method

Consideration of equations (2) and (18) shows that in general,

$$-\frac{dr}{dt} = \text{constant.}\ r^{0.4}(r^2 + a^2)^n \qquad \ldots\ldots (24)$$

For two different radii, $-\frac{dr_1}{dt} = \text{constant},\ r_1^{0.4}(r_1^2 + a^2)^n$

and $-\frac{dr_2}{dt} = \text{constant},\ r_2^{0.4}(r_2^2 + a^2)^n.$

$$\therefore \frac{\frac{dr_1}{dt}}{\frac{dr_2}{dt}} = \frac{r_1^{0.4}(r_1^2 + a^2)^n}{r_2^{0.4}(r_2^2 + a^2)^n} \qquad \ldots\ldots (25)$$

By taking logarithms of both sides of equation (25), it is readily shown that

$$n = \frac{\log\left(\frac{dr_1}{dt}\right) - \log\left(\frac{dr_2}{dt}\right) + 0.4\left\{\log r_2 - \log r_1\right\}}{\log(r_1^2 + a^2) - \log(r_2^2 + a^2)} \qquad \ldots\ldots (26)$$

Data for substitution in the right hand side of equation (26) can be obtained from a plot of radius r versus time t for a given cylinder rotating at constant speed in acid solution: the slopes of the tangents $\left(\frac{dr}{dt}\right)$ corresponding to different values of r are measured and suitable pairs of values of r (r_1 and r_2) together with the corresponding values of $\left(\frac{dr}{dt}\right)$, i.e., $\left(\frac{dr_1}{dt}\right)$ and $\left(\frac{dr_2}{dt}\right)$ are substituted in equation (26).

It must be stressed that the specific rate constant k for a reaction subject to chemical control should be independent of cylinder diameter. Consequently equation (4) and its integrated forms, such as equation (7) (for first order equations) and equation (12) (for second order equations), should be applicable to activation controlled reactions. On the other hand,

equation (18) and its integrated forms should hold for diffusion controlled reactions, provided of course that the equation (15) is applicable. In the case of chemically controlled reactions, it must be borne in mind that the area term in equation (3) is A*, the true surface area, in place of the usually measured apparent area A. The subsequent equations can be developed provided A* is directly proportional to A throughout the measured course of reaction.

SECTION IV

Discussion of Results

IV(a) Hydrochloric Acid

The results, presented in Section II(c) and II(e), of experiments with magnesium cylinders of diameter about 2 cm., revolving at fairly low speeds in 0.033 M hydrochloric acid at temperatures of 25.4, 35.4 and 44.2°C show that the reaction is of the first order with respect to the concentration of acid over an appreciable part of its course. Kilpatrick and Rushton[39a] have shown that the reaction at 25°C with a magnesium cylinder (of unspecified diameter) revolving at 600 r.p.m. is of the first-order over the concentration range 0.01 M to 0.12 M hydrochloric acid. Furthermore, the results of weight-loss experiments presented in Section II(i) support the findings of Kilpatrick and Rushton, and of Roald and Beck referred to earlier, that the reaction is of the first order in acid concentration up to a concentration of about 0.1 M at low speeds of revolution.

The values for the temperature coefficient of reaction $k_{35.4}/k_{25.4}$, 1.24, and for the apparent activation energy of 4.1(7) kilocalories per mole suggest that the reaction between the dilute acid and magnesium is diffusion controlled. However, these results are not in agreement with the results of Kilpatrick and Rushton[39b] over the same temperature range, who calculated for dilute acid a temperature coefficient (k_{35}/k_{25}) of 1.75 and an apparent energy of activation of 10.2 kcal per mole, the latter figure especially suggesting chemical control. Further evidence that the reaction between dilute hydrochloric acid and the curved surface of magnesium cylinders at 25°C is diffusion-controlled is provided by our observations recorded in Section II(f) concerning the dependence of k on cylinder diameter. No such dependence would be expected for a chemically controlled heterogeneous reaction.

The value of the first-order unit rate constant for the dilute acid/magnesium reaction at 25°C agrees fairly well with those of King and Cathcart[30] shown in Table 52.

Table 52

Initial Concentration of $MgCl_2$ (Normality)	Unit Rate Constant k (cm/min) King and Cathcart	Unit Rate Constant k (cm/min). Present work
0	0.497; 0.497	~~0.483~~ 0.461
0.097	0.596	
0.194	0.621	
0.291	0.647	
0.388	0.647; 0.611	
0.486	0.596	

The value in the third column was calculated from measurements of the volume of hydrogen evolved in the reaction, while King and Cathcart used the results of weight-loss determinations to calculate their constants by means of the equation $k = \frac{2.303\ V}{At} \log_{10}\left(\frac{a}{a - x}\right)$. They used cylinders 2.6 cm. long and as reaction vessel they had a 400 c.c. beaker with 250 c.c. of hydrochloric acid of initial concentration 0.050 M in each experiment. The time of their runs varied from 5 to 15 minutes. They did not quote exact values for the radii of their cylinders, but merely stated that the initial diameters were between 1.8 and 2.0 cm, and that the speed of revolution of each cylinder was adjusted so that the surface speed was 2,000 cm/minute. This means that the speeds of revolution of their cylinders must have been in the range 318 to 354 r.p.m. For this reason we cannot make an exact comparison of their results with ours. However, the following calculation will serve as a basis for comparison.

The rate constant (0.461 cm/min) quoted in Table 52 relates to cylinders of diameter 2.0 cm rotating at 200 r.p.m. in 0.033 M hydrochloric acid. Assuming that for a given cylinder diameter, $k \propto s^{0.6}$, then for a speed of 318 r.p.m. (required for a surface speed of 2000 cm/min with a 2 cm cylinder) the unit rate constant for our cylinders would be

$$k_{318}^{2.0} = k_{200}^{2.0} (318/200)^{0.6} = 0.59(5) \text{ cm/min}$$

Assuming further that $k \propto d^{0.4}$

$$k_{200}^{1.8} = k_{200}^{2.0} (0.9)^{0.4} = 0.43(2) \text{ cm/min}$$

whence $k_{354}^{1.8} = 0.432\ (354/200)^{0.6} = 0.60(9)$ cm/min

Thus these estimated results (based upon assumed trends reported elsewhere in the thesis as experimental findings) are in fair agreement with King and Cathcart's result.

These figures, all relevant to the condition $[Mg^{2+}]_o = 0$, do not agree however with the rate constant (corrected to comparable conditions) reported by Kilpatrick and Rushton. These latter workers present data, not for a 2 cm cylinder, but for one with d = 0.8 cm rotated at 800 r.p.m. in initially 0.051 M hydrochloric acid at 25°C. Their value of k was 1.46 cm/min. By calculations similar to those above, their comparable figure for $k_{318}^{2.0}$ is 1.21 cm/min.

Consideration of our k values determined for the curved and for the end surfaces of the cylinders reveals a complex situation. Theoretically if the disc formula of Levich (Section I, 14) and that of Eisenberg, Tobias and Wilke (Section III(d), 17) could be applied to the same system, then it is easily seen that approximately $k(LEV/k(ETW) \approx 5s^{-0.2}$

for diffusion controlled reactions between 2 cm cylinders and dilute aqueuous solutions. Although the two equations apply to different flow characteristics we have partial experimental agreement with this approximation in that little variation is apparent in the ratio R ($= k_{end}/k_{curved}$) with S at 25°C. For example, with 0.0659 M hydrochloric acid, $R_{200} = 1.3$ and $R_{1000} = 1.2$. However we do find that R_{200} becomes progressively less as [HCl] is increased; e.g. at 0.5 M acid $R_{200} \approx 0.9$ and at 1.45 M $R_{200} = 0.5$. These experimental trends may be consistent with near-diffusion control with 0.0659 M HCl; and with a situation involving more concentrated acid where the faster surface velocity of the curved surface begins to lift diffusion control for this surface at a lower r.p.m. than for the flat end. Finally of course, if chemical control were closely approached, by faster stirring or greater concentration of acid or by ultrasonic irradiation, the two surfaces should give similar k values (virtually k_c). In fact the 'curved surface' results of Table 27, the 'end' results of Table 31 and the 'ultrasonic' results given later in Table 54 may all tend to approach a unit rate constant of about 4.5 cm/min for high concentrations and high speeds.

Since it therefore appears that the reaction of magnesium with dilute hydrochloric acid is largely diffusion controlled, a direct measurement of k_c is impossible. Hence an attempt may be made to apply Roller's method to the present work and to that of Centnerszwer[65], as follows.

The results for 0.0659 M hydrochloric acid at 25°C (Table 27, Section II(1)) can be represented by a smoothed equation

$$\log_{10}k = 0.618 \log_{10}s - 1.727 \quad \ldots\ldots (1)$$

From this $k_{200} = 0.4958$, $k_{350} = 0.7008$ and $k_{475.1} = 0.8467$ cm/min. With $s_1 = 200$ r.p.m., $s_2 = 475.1$ r.p.m., $m_1 = 0.007153$ and $m_2 = 0.006109$ whence $B = 0.007368$.

Using the value of k at the intermediate speed of 350 r.p.m.,

$$k_c = -0.007368 \times 108.4 \times 2.303 \log_{10} \left[1 - \frac{0.7008}{0.007368 \times 108.4} \right]$$

$$= 1.68 \text{ cm/min.}$$

Centnerszwer's results with magnesium and 0.125 M hydrochloric acid at 25°C are included in Table 53.

Table 53

S r.p.m.	k cm/min
50	0.36
100	0.41
200	0.67
400	0.95
750	1.43
855	1.72

A least squares treatment of these data leads to the equation:

$$\log_{10} k = 0.5606 \log_{10} S - 1.452 \qquad \ldots\ldots \quad (2)$$

If $(S_2/S_1)^{0.8} = 2$ and $S_1 = 200$ r.p.m., $S_2 = 475.6$ r.p.m. By equation (2) $k_{200} = 0.688$ cm/min and $k_{475.6} = 1.118$ cm/min.

$\therefore$ $m_1 = 0.009926$, $m_2 = 0.008067$ and $m_1/m_2 = 1.2304$,

whence B = 0.01048 (Roller[9] finds B = 0.010). Using the value of k_{350} calculated by equation (2) there is obtained

$$k_c = -2.303 \times 0.01048 \times 83.41 \log_{10} \left[1 - \frac{0.7835}{0.01048 \times 83.41} \right]$$

$$= 1.98 \text{ cm/min.}$$

Hence there is a fair agreement between the values found for k_c from our data and from the data of Centnerszwer. However Roller claims to have calculated a value of 2.80 cm/min for k_c from Centnerszwer's results.

If in equation (39), Section III(b), the exponent on s is taken to be 0.7 instead of 0.8, equation (40) of the same section is modified to:

$$k_c = Bs^{0.7} \left(1 - \exp. \left[- k_{c/Bs^{0.7}} \right] \right) ,$$

and by calculations similar to those performed above the value found for k_c with our data is 2.19 cm/min, while Centnerszwer's data lead to a value of 2.43 cm/min. Thus k_c(calc) varies rapidly with the assumed exponent.

In accordance with the suggestion put forward in Section III(a) the experiments with ultrasound were performed in an effort to obtain conditions in which the reaction between magnesium and hydrochloric acid is chemically controlled, thereby enabling a direct experimental determination of k_c to be made. The temperature coefficient of the ultrasonically influenced reaction between 0.0659 M hydrochloric acid and magnesium recorded in Section II(g) indicates a partly or wholly diffusion-controlled reaction. Similarly the temperature coefficient recorded in Section II(g), page 72 is indicative of a diffusion controlled reaction, although for some reason this value is rather low.

In addition to the application of ultrasound, the stirring speed and the concentration of the acid were increased in the hope that the combined effect would bring about a change of control in the reaction. The results of Section II(h) show that the rate with 0.0659 M hydrochloric acid and magnesium cylinders in the absence of ultrasound increases considerably with stirring speed (an almost six-fold increase in speed caused an increase of about 270% in the rate of reaction), but that the same increase in speed produced only about a 15% increase in the ultrasonically influenced rate. The relative rate figures reflect this. Therefore increased speed of revolution, with this concentration of acid, does not alter the effectiveness of the ultrasonic waves very much. With 2.89 M

hydrochloric acid, an increase in stirring speed from 2,500 r.p.m. to 5,500 r.p.m. caused an increase of about 60% in reaction rate in the absence of ultrasound, while a similar change in speed of revolution in the ultrasonically influenced reaction caused about a 27% increase in reaction rate. Data recorded in Tables 19 and 21 were used to calculate first order unit rate constants for the ultrasonically influenced reaction, the values being recorded in Table 54. These figures show that, at a given cylinder speed, variation of acid concentration over a fairly wide range does not

Table 54

Cylinder Speed (r.p.m.)	Unit Rate Constant k (cm/min)							
	0.3295 M	0.659 M	1.170 M	1.44 M	1.441 M	1.45 M	2.88 M	2.89M
200	3.82	3.92	3.80			3.74		
1,000				4.40			4.28	
2,500				3.52				3.43
4,000				3.55				3.65
5,500					4.19			4.27

affect very much the value of the unit rate constant. Moreover variation of cylinder speed at a given initial concentration of acid does not alter the unit rate constant to a great extent. It seems reasonable to suggest that the ultrasonic waves have brought about a change to near chemical control and that the unit chemical rate constant has a value of about 4.4. cm/min at 25°C which, however, is nearly twice the mean of the values for k_c calculated from our results and those of Centnerszwer by the method based on Roller's equation.

Another method which can in principle be used to calculate k_c is by the use of equation (13) of Section III(b). Of the quantities on the right hand side of this equation c, A, V and $\frac{dc}{dt}$ can readily be obtained from our

experimental results; but uncertainties exist concerning the values to be assigned to δ, D, σ and A*. Concerning absolute areas A* of metallic surfaces, some work carried out by T.L. O'Connor and H.H. Uhlig[66] using a gas adsorption method, based on the B.E.T. equation, with ethane as adsorbate at - 183°C has yielded some interesting results, some of which are included in Table 55. Their roughness factor was defined by the ratio Absolute Area/Apparent Area.

Table 55

Specimen	Surface Preparation	Area (cm^2)		Roughness Factor
		Geometrical	Absolute	
Armco Iron Sheet	Hydrogen - reduced at 1,000°C	200	244	1.22
Armco Iron Steel	Hydrogen - reduced at 1,000°C	200	257	1.29
Armco Iron Sheet	Abraded 2/0 emery, degreased in benzene	41,1	138	3.4
18-8 Stainless Steel	Electropolished	115	129	1.12

The small values obtained for the roughness factor in most cases seem rather surprising. R. Davis, T. Dewitt and P. Emmett[67], using krypton, butane and Freon as adsorbates, reported roughness factors of 1.10 to 1.37 for silver foil and 1.07 to 1.64 for Monel foil, depending on the gas used. Even more surprising is the fact that Rhodin[68] reported that abraded and electropolished copper had a roughness factor of about unity. It is difficult to estimate a value for σ, although for dilute solutions it may not be far short of unity[69]. Much uncertainty exists about the value to be assigned to D for this reaction. One can make a theoretical estimate if it is assumed that the proton diffuses to the magnesium surface as a definite entity such as $H_9O_4^+$. The existence of this complex was first suggested by

Wicke, Eigen and Ackermann[70], and a few years later Beckey[71] presented evidence from mass spectrometer studies, for its existence in the vapour phase. It appears to have a tetrahedral configuration and from data collected by B.E. Conway[72] one can estimate an effective radius for it of about 3.5 Å. According to J.T. Edward[73] a tetrahedral molecule can be regarded as being equivalent to a sphere for the purpose of calculating diffusion coefficients by the Stokes-Einstein equation:

$$D = kT/6\pi\eta r \qquad \ldots\ldots (3)$$

where k is Boltzmann's constant; T is the absolute temperature; r is the effective radius of the molecule; and η the coefficient of viscosity of the solution. For dilute hydrochloric acid at 25°C, η = 0.009 poise and using r = 3.5 Å equation (3) gives a value for D of 6.9×10^{-6} cm²/sec. This value, however, is unexpectedly small when compared to the measured value for dilute acid, about 3.06×10^{-5} cm²/sec at 25°C, diffusing into water. Indeed according to the work of J.W. McBain and J.R. Vinograd[74] one might expect hydrogen ions to have a diffusion coefficient greater than 3.06×10^{-5} cm²/sec as they diffuse against magnesium ions produced at the metal surface. McBain and Vinograd found that when decinormal aqueous hydrochloric acid was diffused at 25°C against decinormal aqueous potassium chloride, the diffusion coefficient for hydrogen ions was 4.40 cm²/day as compared with 2.54 cm²/day for hydrochloric acid alone into water, i.e. a ratio of 1.73. King and Cathcart have shown that the diffusion coefficients of strong acids such as hydrochloric and perchloric acid are increased by the addition of salts, relatively small increases in salt concentration causing marked increases in the diffusion coefficients; but that diffusion coefficients of weak acids such as acetic and formic acids are hardly affected by the addition of salts.

Concerning the value to be assigned to δ, a survey of the literature[13a] on heterogeneous reactions between solids and liquids has shown that the thickness of the diffusion layer varies from about 2×10^{-3} to about 4×10^{-3} cm at room temperatures. The value of δ can be calculated for a rotating disc from known properties of the system when the fluid is in laminar flow, both when the heterogeneous reaction is entirely diffusion controlled and when it is in the regime of intermediate kinetics[75]. In the case of a rotating cylinder, however, the value of δ could be calculated in the case when the reaction at the curved surface is entirely diffusion controlled within the Reynold's Number range of 1,000 to about 100,000, but it is not known (see below) whether Eisenberg, Tobias and Wilke's formula can be applied to the case when a reaction is in the intermediate regime.

In view of the uncertainties involved in assigning values to A*, σ, D and δ, one cannot rely on values of k_c calculated by means of equation (13) or equation (19) of Section III(b) . However, it would be interesting to substitute values of k_c found by other methods, e.g. by Roller's method, in either equation in order to find whether reasonable values of D/δ are obtained. Thus in one of our experiments, a magnesium cylinder of length 3.95 cm was rotated at 1,000 r.p.m. in 3,000 c.c. of 0.0659 M hydrochloric acid for five minutes and it experienced a loss in weight of 0.112 gram, the temperature being 25°C. The mean area of the exposed curved surface was 23.08 sq. cm. Using the integrated form of the first-order rate equation, the value of the overall constant k was found to be 0.02065 cm/sec. Assume that k_c = 0.02833 cm/sec, a value found from our results using Roller 's method. Let $\delta/D = x$. The mean concentration c = 0.002347 gm/c.c. and $\frac{dc}{dt} = -3.715 \times 10^{-7}$ gm/cc/sec. Furthermore, assume that $\sigma = 1$ and A* = A. Substituting these values in equation(13), Section III(b)

we have,

$$0.02833 = \frac{130 \times 3.715 \times 10^{-7}}{[0.002347 - (130 \times 3.715 \times 10^{-7} x)]},$$

whence $x = 13.29$, i.e. $\frac{D}{\delta} = 0.07525$.

If we assume at $\delta = 0.003$ cm., then $D = 2.26 \times 10^{-4}$ cm^2/sec. The accepted value of D for hydrochloric acid[76] at 25°C is 3.06×10^{-5} cm^2/sec, so that the value just calculated for D seems too high. Even if the value of δ is assumed to be 0.0015 cm, then $D = 1.13 \times 10^{-4}$ cm^2/sec which again seems too high, even allowing for an electrolyte effect such as was found by McBain and Vinograd.

Assuming that $k_c = 0.07333$ cm/sec, the value suggested by our work on the ultrasonically influenced reaction, then we have

$$0.07333 = \frac{130 \times 3.715 \times 10^{-7}}{[0.002347 - 4.83 \times 10^{-5} x]},$$

whence $x = 34.95$,

or $D/\delta = 0.02861$ cm/sec.

If $\delta = 0.003$ cm, $D = 8.584 \times 10^{-5}$ cm^2/sec. Now supposing $\sigma A^* = 1.2$ A, which seems reasonable considering the values of the roughness factors for various surfaces quoted in Table 55 , then we have

$$0.002347 - 4.83 \times 10^{-5} x = \frac{130 \times 3.715 \times 10^{-7}}{1.2 \times 0.07333},$$

whence $x = 37.24$,

or $D/\delta = 0.02685$.

If $\delta = 0.003$ cm., $D = 8.053 \times 10^{-5}$ cm^2/sec, whereas a value for δ of 0.0015 cm would give D a value of 4.026 cm^2/sec which seems reasonable.

We shall now discuss the results obtained with more concentrated hydrochloric acid reacting with magnesium cylinders. In Section II(i) we noted the evidence pointing to the fact that the reaction appears to have no simple order beyond an acid concentration of about 0.15 M, in approximate

agreement with the findings of Roald and Beck[49]. Although the latter workers claimed that at an acid concentration of about 1.4 M the curves obtained by plotting rates $(\frac{dc}{dt})$ against concentration for the reaction at the curved surface of cylinders at a number of rotational speeds up to 6,400 r.p.m. converged, i.e. the rate is unaffected by rotational speed, we found no evidence of a convergence at this concentration, as was noted in Section II(j). At higher concentrations of acid, hydrogen evolution becomes vigorous, and Roald and Beck suggested that the breaks in the plot of rate versus concentration were caused by the stirring action of the hydrogen bubbles. They pointed out that the temperature increases in their experiments cannot account for all the increase in rate, e.g. at a cylinder speed of 947 r.p.m. in 0.5 M hydrochloric acid, the dissolution rate was 80% higher than it would have been if there were no break in the graph; if local heating were the cause, this increase would have required a temperature rise of about 25 Centigrade degrees, but the actual temperature difference was only 3.5 Centigrade degrees. This explanation is consistent with the observation that the effect of the rate of stirring becomes less as the dissolution rate (and with it, the rate of hydrogen evolution) increases. Presumably at the lower dissolution rates the comparatively few small hydrogen bubbles are able to diffuse through the diffusion layer without causing much stirring and consequent disruption of concentration gradients, whereas at the higher dissolution rates the bubbles produced can cause considerable stirring of liquid and, therefore, increase the rate of reaction. Powerful ultrasonic waves might cause so much additional stirring near the metal/solution interface that concentration gradients are effectively removed.

The results from experiments with the more concentrated acid recorded in Section II(l) can be used to calculate rough values of temperature coefficients. Thus using the values of the apparent rate constants listed in

Table 27 of that Section, the values for temperature coefficients included in Table 56 were calculated. Some results for 0.0659 M hydrochloric acid are also included for comparison. It is realised that the rate constants for such dilute acid as this are true first-order rate constants, so that probably more reliance can be placed on the values of the temperature coefficients for the reaction with this acid than on the values calculated for the more concentrated acid. For 1.45 M acid the values in the fourth column of Table 56 are not far short of 2, the value to be expected of a chemically-controlled reaction; and similarly for the 1.9 M acid. However, the values of the temperature coefficients for the reaction between magnesium and 1.17 M and 0.0659 M acid suggest a diffusion-controlled reaction. The temperature coefficients calculated from the results for cylinders of diameter about 1.2 cm. revolving in 0.503 M

Table 56

Approximate Temperature Range °C.	Concentration of Acids (M)	Cylinder Speed R.p.m.	Temperature Coefficient (corrected when necessary to a 10° interval)
14 to 4	1.45	200	1.9
	"	1,000	1.8
	"	4,000	1.6
15 to 25	1.17	1,000	1.5
14 to 25	0.0659	200	1.5
	"	1,000	1.4
	"	4,000	1.4
4 to 14	1.45	200	2.0
	"	1,000	1.7
	"	4,000	1.7
5 to 15	1.9	1,000	1.9
"	"	4,000	1.6
4 to 14	0.0659	200	1.3
	"	1,000	1.4
		4.000	1.4

hydrochloric acid at 15.5 and 25.5°C seem to indicate a diffusion-controlled reaction: at each of the speeds 200, 500 and 800 r.p.m. the

temperature coefficient has the same value, viz., 1.3. From the data on the reaction at the flat end of 2.0 cm. diameter cylinders given in Table 30, the mean temperature coefficient for 0.330 M acid over the temperature range 5.4° to 25.5°C = $(0.86/0.45)^{\frac{1}{2}}$ = 1.38, a value suggesting diffusion control for the reaction. The data in Table 31 on the reaction at the flat ends of 1.0 cm. diameter cylinders revolving in 1.45 M acid lead to values of 1.5 and 1.6, respectively, for the temperature coefficient at 1,000 and 5,500 r.p.m. over the temperature range 15.5 to 25.5°C.

It is interesting to note from Table 30 that the first-order rate constant k has a fairly constant value of 0.6 to 0.7 cm/min over the approximate concentration range of 0.0165 to 0.16 M acid, but that the calculated value then rises appreciably with increasing initial concentration of acid - another demonstration that the reaction is of the first order up to about 0.2 M acid.

The results reported in Section II(k) of the reaction between magnesium and about 1 M (initially) hydrochloric acid in which cylinder diameters decreased appreciably apparently support the other evidence which suggests higher apparent orders of reaction in more concentrated acid. We obtained the data within the Reynold's Number range of 1,000 to about 100,000 and assumed that $k \propto r^{0.4}$, a relation deduced in Section III(d) from Eisenberg, Tobias and Wilke's equation. However these investigators worked with dilute solutions and their unit rate constants k were first-order constants determined for reactions which were diffusion controlled. In about 1 M hydrochloric acid where the reaction has an apparent order between 1 and 2, it is not certain whether the general equations

$$X_n = \frac{1}{t} \int_{r_2}^{r_1} \frac{dr}{r^{0.4} (r^2 + a^2)^n} \quad , \text{ where } X_n = \text{constant,}$$

and $-\frac{dr}{dt} = \text{constant, } r^{0.4} (r^2 + a^2)^n$ obtained in Section III(d)

can be applied. However, provided that one works in the Reynold's Number range of 1,000 to 100,000, these equations may well hold, perhaps with a slight modification to the exponent 0.4. It would be interesting to investigate the reaction between magnesium and hydrochloric acid in the presence of a depolariser in order to determine whether, in the absence of complications due to the stirring action of hydrogen bubbles, the reaction continues to be of the first order with respect to acid concentration in more concentrated acid. Unfortunately no data are available in the literature to test this.

Of interest is the fact that J. Marangozis and Johnson[77] have suggested that mass transfer data can be satisfactorily correlated by an equation based on the Gilliland-Sherwood[78] correlation, which is

$$Sh = a\,(Sc)^{b}\,(Re)^{c} \qquad \ldots\ldots \quad (3)$$

where Sh is Sherwood's Number defined by Sh = kl/D, k being the mass transfer coefficient, l the diameter of the (cylindrical) containing vessel and D the diffusion coefficient of the solute. Eisenberg, Tobias and Wilke based their equation on the Chilton-Colburn correlation[79]

$$k/_{u} = (Sc)^{-2/3}\,\phi\,(Re) \qquad \ldots\ldots \quad (4)$$

where u = the peripheral velocity of the cylinder and ϕ (Re) a function of the Reynold's Number. Marangozis and Johnson's equation is

$$kl/D = 0.635\,(Sc)^{1/3}\,(Re)_{h}^{0.7} \qquad \ldots\ldots \quad (5)$$

where $(Re)_h$ is the Reynold's Number based on gap width h between the inner rotating cylinder and the outer coaxial cylindrical container,

$(Re)_h = sdh/\nu$, where s = number of revolutions/sec., d = cylinder diameter and ν = kinematic viscosity of the solution. In

Eisenberg, Tobias and Wilke's equation:

$$k/_u = 0.0791\ (Sc)^{-0.644}(Re)^{-0.30} \qquad \ldots\ldots\ (6)$$

the Reynold's Number (Re) = ud/ν . Marangozis and Johnson claim that a Gilliland-Sherwood type of correlation should be more appropriate because it would encompass all the variables, whereas a Chilton-Colburn type of correlation does not include l or h. However, as shown in Section II(f) we found a satisfactory correlation of our data on the reaction between magnesium and dilute hydrochloric acid by using Eisenberg, Tobias and Wilke's equation.

IV(b) Results of Experiments with Acids other then Hydrochloric Acid

Table 57 compares the values of our unit first-order rate constants k for the reactions at 25°C between magnesium cylinders and acetic, formic, citric and benzenesulphonic acids, respectively, with those obtained by King and Cathcart[30] for the same reactions. The latter workers used cylinders of diameter about 2 cm., whereas in our experiments with formic, citric and benzenesulphonic acids we used cylinders of diameter about 2.5 cm. In our experiments with acetic acid the cylinders used had a diameter of about 2 cm. The agreement between the values of the rate constants in the case of acetic acid is good, while the agreement between our values of k and the values of King and Cathcart for formic and citric acids can be considered to be fairly good. However, there is a discrepancy in the results for benzenesulphonic acid. It may be significant that the curved surface of the cylinders used in our experiments with this acid were markedly scored by the reaction, whereas this roughening was not found with other acids.

In Table 58 are compared values of the chemical rate constants k_c at 15° and 25°C for the reactions between magnesium and the various acids listed in this Table. All of these values except one with hydrochloric acid at 25°C were calculated with the exponent 0.8 on S in Roller's equation. In general the calculated values of k_c rise as the exponent (y) on S is decreased. For example, using the experimental results for 0.2923 M formic acid and magnesium at 25°C reported in Section II(1), it can be shown that the value of k_c increases from 0.613 cm/min at y = 1 to 1.152 cm/min at y = 0.7 :

Table 57

Acid	Initial Concentration (M) of Acid		Initial concentration (N) of Magnesium Salt	Unit rate Constant k (cm/min), Ours	Unit Rate Constant k (cm/min) King and Cathcart
	Our experiments	King and Cathcart			
Acetic	0.5288	0.0597	0	0.182	0.186, 0.177, 0.182
			0.10		0.177
			0.20		0.177
			0.30		0.182
			0.40		0.167
Formic	0.2937	0.0582	0	0.311	0.236, 0.220, 0.227
			0.112		0.236
			0.223		0.225
			0.335		0.197
			0.446		0.197, 0.173
Citric	0,4726	0.1833	0	0.129	0.139
			0.20*		0.146
			0.40*		0.146
			0.60*		0.154
Benzenesulphonic	0.3994	0.050	0	0.99	0.518, 0.499, 0.502
			0.10		0.604
			0.20		0.616
			0.30		0.592

k values in the fifth column adjusted to a cylinder speed of 340 r.p.m.

* King and Cathcart used sodium chloride in these experiments.

Table 58

Acid	Dissociation Constant K_A at 25°C	$\text{Log}_{10} K_A$	k_c (cm/min.) calculated by Roller's Method		$\text{Log}_{10} k_c$	
			15°C	25°C	15°C	25°C
Acetic	1.75×10^{-5}	- 4.757	0.256	0.413	- 0.592	- 0.384
Formic	21.4×10^{-5}	- 3.670	0.779	0.836	- 0.109	+ 0.012
Citric	73.0×10^{-5} (K_1)	- 3.137	0.0713	0.154	- 1.147	- 0.813
Salicylic	125.0×10^{-5}	- 2.903	-	0.424	-	- 0.373
Benzenesulphonic	279.0×10^{-5}	- 2.554	1.00	1.84	0.000	+ 0.265
Hydrochloric	50(?)	+ 1.7		1.83*		+ 0.263
				2.32$^{\Delta}$		+ 0.365

* Mean of cour value and Centnerszwer's with exponent on s of 0.8 in Roller's equation

$^{\Delta}$ " " " " " " " 0.7 " "

If $y = 1$, $k_c = -0.001239 \times 350 \times 2.303 \log_{10}\left(1 - \frac{0.328}{.001239 \times 350}\right) = 0.613$ cm/min

If $y = 0.9$, $k_c = -0.002038 \times 194.8 \times 2.303 \log_{10}\left(1 - \frac{0.3280}{.002038 \times 194.8}\right) = 0.695$ cm/min.

If $y = 0.8$, $k_c = -0.003367 \times 108.4 \times 2.303 \log_{10}\left(1 - \frac{0.3280}{.003367 \times 108.4}\right) = 0.836$ cm/min

If $y = 0.7$, $k_c = -0.005621 \times 60.38 \times 2.303 \log_{10}\left(1 - \frac{0.3280}{.005621 \times 60.38}\right) = 1.152$ cm/min

If $y = 0.6$, k_c indeterminate.

For all these calculations, s_1 was chosen to be 200 r.p.m. and $k_{350} = 0.3280$ cm/min was used as a mid-value. It is concluded, however, that the calculated value of k_c would rise asymptotically as the value for y approached 0.645, the observed slope correlating $\log_{10} k_{obs}$ and $\log_{10} s$ in the equation:

$$\log_{10} k_{obs} = 0.645 \log_{10} s - 2.125,$$

giving k_{obs} in cm/min. Thus if $y = 0.66$, k_c is calculated to be 1.56 cm/min. Hence if y is near the observed slope correlating $\log_{10} k_{obs}$ and $\log_{10} s$, this method of calculation could lead to unsure results.

If a statistical correction is applied to the Brönsted-Pedersen relationship (see below), there is obtained[39]

$$k_a = G_1 K_A^x q^x p^{1-x} \qquad \ldots\ldots \quad (7)$$

where K_A is the acid dissociation constant, p is the number of ionizable hydrogen atoms in the molecule, q is the number of positions at which a proton can be attached in the molecule of the conjugate base, and G_1 and x are constants ($0 < x < 1$). If the acids under investigation conform to this equation, a plot of $\log_{10}(k_a/p)$ versus $\log_{10}\left(\frac{q}{p} K_A\right)$ should give a straight line with a slope x and an intercept G_1. In Table 59 are summarised the data necessary to test this relationship.

Table 59

Acid	q	p	$\log_{10}(q\ K_A/p)$ at 25°C	$\log_{10}(k_c/p)$ at 25°C
Acetic	2	1	- 4.456	- 0.384
Formic	2	1	- 3.369	+ 0.012
Citric	2	3	- 3.313	- 1.290
Salicylic	2	1	- 2.602	- 0.373
Benzenesulphonic	3	1	- 2.077	+ 0.265
H_3^+O	1	1	+ 1.7	+ 0.263 and + 0.366

The values of k_c and K_A were taken from Table 58. If the values of $\log_{10}(q\ K_A/p)$ in Table 59 are plotted against the corresponding values of $\log_{10}(k_c/p)$, the points do not fall near a straight line, so that there is no Brönsted-Pedersen relationship in this case.

It is of course realised that for the conditions obtaining in our experiments, the use of Roller's method may not lead to true values for k_c. Thus Roller gives as a condition for neglecting all terms except the first, with an error < 1%, in equation (29) of Section III(b), the inequality $Dt/L^2 \geqslant 0.2$; but under the conditions of the experiments described in this work (and for most of the experiments of other investigators in this field) Dt/L^2 has values considerably less than 0.2. For example, take an experiment in which a magnesium cylinder with an exposed area of 25 sq.cm. rotates for 30 minutes in 300 c.c. of hydrochloric acid ($D = 3.1 \times 10^{-5}$ cm^2/sec), then $Dt/L^2 = 3.88 \times 10^{-4}$. Again Roller used Centnerszwer's[65] results for the magnesium/hydrochloric acid reaction to calculate a value for k_c, but the conditions in Centnerszwer's experiments were such that the value of Dt/L^2 was of the order of only

10^{-5}. Furthermore the condition given by Roller for equating $\bar{B}_1$ to unity in arriving at equation (34) of Section III(b) is the inequality $k_c L/D < 1$, but for the usual experimental conditions the value of $k_c L/D$ is considerably greater than one. In fact for the experiments reported here $\frac{Dt}{L^2} \simeq 0$ and $kL/D \longrightarrow \infty$. It is of interest to note that our work on the ultrasonically influenced reaction between magnesium and hydrochloric acid suggests that the values for k_c calculated by Roller's method may be too low.

We still have to consider the possibility that, for the acids investigated in this work, no Brönsted-Pedersen relationship would be expected for reasons connected with differences in molecular structure and not merely because Roller's method may not give true values for k_c. Therefore a general discussion of the circumstances under which these relationships are expected to hold and also of those under which deviations might be expected to occur will now be given.

Kilpatrick and Rushton[39] point out that if the heterogeneous reaction between magnesium and an acid is chemically controlled, there should be a relationship between the observed rate constant k and the thermodynamic dissociation constant K_A of the acid of the type first suggested by Brönsted and Pedersen[80] to correlate data on acid-base catalysis

$$k = G_A K_A^{\alpha} \qquad \ldots\ldots \quad (8)$$

where G_A and α are constants, with $0 < \alpha < 1$. As acid-base catalysis involves the transfer of a proton either from a molecule of acid catalyst or to a molecule of basic catalyst, it seems natural to seek a relationship between the effectiveness of the catalyst and its acid (or basic) strength, the strength in aqueous media being a measure of the ease with which the catalyst transfers a proton to or from a molecule of water. H.S. Taylor[81] was first to suggest a relationship

between the catalytic constant k_a and the acid dissociation constant K_A:

$$k_a = k_{H^+} K_A^{\frac{1}{2}} \quad \ldots\ldots \quad (9)$$

where k_{H^+} is the catalytic coefficient of the hydrogen ion H_3O^+. Equation (9), however, agreed only very approximately with the experimental data. Then ten years later the Brönsted-Pedersen relationship, i.e. equation (8) was proposed. R.P. Bell[82] has shown that in general the same type of relationship applies to prototropic reactions whether or not there is a pre-equilibrium with the catalyst. Provided a series of chemically similar catalysts is used with the same substrate, a Brönsted-Pedersen relationship would be expected to represent the data adequately. For example, Bell and Higginson[83] studied, by a dilatometric method, the acid-catalysed decomposition of acetaldehyde hydrate in aqueous acetone and used as catalysts a series of forty five monocarboxylic acids and phenols the strengths of which in water ranged over ten powers of ten. Their observed catalytic constants follow a Brönsted-Pedersen relationsip with the exponent $\alpha = 0.54$ and a maximum and mean logarithmic deviation of 0.3 and 0.1, respectively.

The simple relationship of equation (8) is for exactness modified by including a statistical correction. Brönsted[84] was the first investigator to give a correct treatment of the statistical correction, although an earlier paper by Brönsted and Pedersen[80] contains the first suggestion of such a correction, but in an incomplete form. If for a given acid-base pair A-B in which p is the number of equivalent protons on the acid molecule and q the number of equivalent positions on B where a proton can be accepted, then the catalytic power of A is related to its observed dissociation constant by

$$\frac{k}{p} = G_A \left(\frac{qK_A}{p}\right)^{\alpha} \quad \ldots\ldots \quad (10)$$

Similarly, for basic catalysis by B, we have

$$\frac{k_b}{q} = G_B \left(\frac{pK_B}{q} \right)^{\beta} \qquad \ldots\ldots (11)$$

where k_b is the catalytic rate constant, K_B is the base dissociation constant, and G_B and β are constants. F.H. Westheimer[85] has developed more complicated equations for those cases in which the various protons or points of attachment are not all equivalent. It is noteworthy that some authors apply the statistical correction only when p and q refer to different atoms in the same molecule, e.g. p = 2 for oxalic acid or the hydrazinium ion $H_3\overset{+}{N}\cdot\overset{+}{N}H_3$, but p = 1 for NH_4^+. The statistical correction was applied by Brönsted and Pedersen[80] to a series of polycarboxylic acids in the acid-catalysed decomposition of nitramide.

Not only might one expect a Brönsted-Pedersen type of relationship to hold in the case of a single substrate and a series of similar catalysts, but also in the case of catalytic reactions where the catalyst remains the same and a series of similar substrates is investigated. Unfortunately it is rarely possible to study the latter type of reaction quantitatively since the substrates concerned are usually such very weak acids or bases that their strengths cannot be measured directly. However, Bell[86] quotes just one example, using the data of R.G. Pearson and R.L. Dillon[87], that of a series of compounds containing the group $\rangle CH\cdot CO-$ the halogenation of which is catalysed by bases. Such compounds are sufficiently strong acids for the direct measurement of pK to be made. A plot of $\log k_1$ versus pK, where k_1 and K refer to the process

$$\rangle CH\cdot CO^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \rangle C : C(O^-)- + H_2O$$

where $K = \frac{k_1}{k_2}$ cf. $HB + H_2O \rightleftharpoons H_3^+O + B^-$,

shows an approximate parallelism between the two quantities, the line having a slope < 1 throughout but showing a definite curvature.

More significant to our case, a Brönsted-Pedersen relationship might be expected to hold for the reactions between a given metal and a series of acids the thermodynamic dissociation constants of which are known. Such reactions are essentially acid-base reactions, the role of the base being played by the electrons in the metal surface and the acid by either the hydrated proton H_3O^+ (or perhaps $H_9O_4^+$) or molecular acid molecules such as $CH_3 \cdot COOH$.

A survey of the experimental results in the chemical literature shows that there are both positive and negative deviations from the Brönsted-Pedersen relationships. Thus in the acid-catalysed dehydration of acetaldehyde hydrate studied by Bell and Higginson, several pseudoacids, i.e. acids the ionization of which involves a considerable electronic rearrangement, exhibited large negative deviations, 2-nitropropane for example showing a logarithmic deviation of - 1.9 units. On the other hand, for the same reaction, acids in which the structures of anion and unionized acid are very similar exhibited positive deviations, diethylketoxime for example showing a logarithmic deviation of + 2.1 units.

The Brönsted-Pedersen relationships are really one form of the so-called linear free-energy relations and can be regarded as a special case of the Hammett[88] equation. Although the Hammett equation dealt originally only with meta- and para- substituted benzene derivatives and does not apply very well to aliphatic compounds, the Brönsted-Pedersen relationships, although limited to the special class of acid-base reactions, do in fact cover a wider range of compounds both in the aliphatic and in the aromatic series. An interpretation of the Brönsted-Pedersen relationships in terms of molecular potential energy curves for the reaction

$$XH + Y \longrightarrow X + HY$$

was given at about the same time by Bell[89], and by Horiuti and Polanyi[90]. Bell[91] has also suggested explanations for certain deviations from the Brönsted-Pedersen relationships in terms of the differences in the shapes of the potential energy curves found among acids or bases of comparable strengths. Deviations from the Brönsted-Pedersen relationship occur in the reactions involving some series of amines, e.g. R.G. Pearson[92] has shown that the rates at which the members of the series NH_3, NH_2Me, $NHMe_2$ and NMe_3 react with nitroethane to form the anion bear no relation to the basic strengths of these amines. An explanation of such anomalies can be found in terms of the interaction of the cations with water. Thus in the series NH_4^+, $MeNH_3^+$, $Me_2NH_2^+$ and Me_3NH^+ such an interaction will vary considerably as the successively introduced alkyl groups act by excluding water molecules from interacting closely with the positive charge, thereby decreasing the stabilisation of the cation. This effect acts in the opposite direction to the inductive effect. Steric hindrance can in some cases cause deviations from the Brönsted-Pedersen relationship, e.g. in the hydration of acetaldehyde catalysed by substituted pyridines and their cations[93], alkyl substituents in the 2- and 6- positions cause a lowering of catalytic power, i.e., a negative deviation. Although substitutions of this kind have little effect on acid-base equilibria because of the small size of the proton, they may affect the rate of an acid-base reaction, since the two species A_1 (the acid) and B_2 (the base) must be close together in the transition state, and large groups in one or both of the reactants may hinder the attainment of this situation.

The discussions of the Brönsted-Pedersen relationships by Bell, and by Horiuti and Polanyi assumed that proton transfer $AH + B \longrightarrow A + HB$ occurs by the classical mechanism, but J.J. Weiss[94] has considered the case where proton transfers occur exclusively by quantum mechanical tunneling. He assumed that transfer takes place along a straight line

joining the centres of the atoms A, H and B. For his calculations he assumed a one-dimensional potential barrier with a width of only 0.4 to 0.6 Å [95] equal to the distance the proton has to travel along the hydrogen bond A--H--B, and was able to show that a Brönsted-Pedersen type of relationship could be derived for this model. It is interesting to note that the extent to which electrochemical proton discharge occurs by quantum-mechanical tunneling has fairly recently been the subject of much discussion[96].

In view of the above discussion of the circumstances under which deviations occur from the Brönsted-Pedersen relationships, and taking into consideration the considerable variation in the structures of the acids used in this study, it would not be surprising to find that these acids did not obey such a relationship. However, it is not possible to check this until reliable values for k_c can be calculated.

It is interesting to observe that recently Marangozis[97] has presented a treatment of the reaction between magnesium and hydrochloric acid in which hydrogen ions from the acid are imagined to be neutralised by hydroxyl ions in a narrow zone away from the actual magnesium surface. He envisages the processes occurring at the interface to be as follows:

Ionization of magnesium atoms $Mg \rightleftharpoons Mg^{++} + 2\varepsilon$ (anode),

accompanied by dissociation of water molecules $2H_2O \rightleftharpoons H_3^+O + OH^-$

while the hydrogen ions are discharged on the surface of the metal

$$2\varepsilon + 2H_3^+O \rightleftharpoons 2H + 2H_2O \text{ (cathode)}$$

$$H + H \rightleftharpoons H_2$$

As the hydrogen ions from the water are discharged at the magnesium surface the excess hydroxyl ions diffuse outwards towards the narrow neutralisation zone, where rapid neutralisation occurs

$$OH^- + H_3^+O = 2H_2O$$

Therefore between the interface and the narrow neutralisation zone there ought to be, on this theory, an alkaline layer and this should show up as a pink zone adjacent to the magnesium surface if phenolphthalein is added to the solution. The situation is as depicted in Figure 24. The unbroken lines in this diagram represent the concentration gradients of the various ionic species present in the solution. In order to test for the presence of an alkaline layer, experiments were conducted in which the surface of a magnesium cylinder dissolving in dilute hydrochloric acid (0.1 M and 0.05 M) in the presence of phenolphthalein was observed through a microscope. However, no pink coloration was discernible, suggesting that no thin layer containing hydroxyl ions exists near the surface. Therefore there is some doubt concerning the validity of Marangozis' theory.

Other interesting theories of heterogeneous reactions between metals and aqueous solutions have from time to time been advanced. For example, G.E. Kimball[98] has approached the problem from an electrochemical point of view, making use of the theory of absolute reaction rates to calculate dissolution currents. In general the rate expressions obtained by him are complicated functions of ionic activities and the (mixed) potential V of the dissolving metal; but in the regime of diffusive control in the case where hydrogen is more "noble" than the dissolving metal (such as magnesium) and when the discharge of metal ions and the solution of hydrogen can be neglected, the rate equation reduces to the simple first-order rate expression,

$$\text{rate} \propto [\text{acid}]$$

an expression which does not involve V. However, the indications are that the kinetics may well be complicated when the reaction moves further

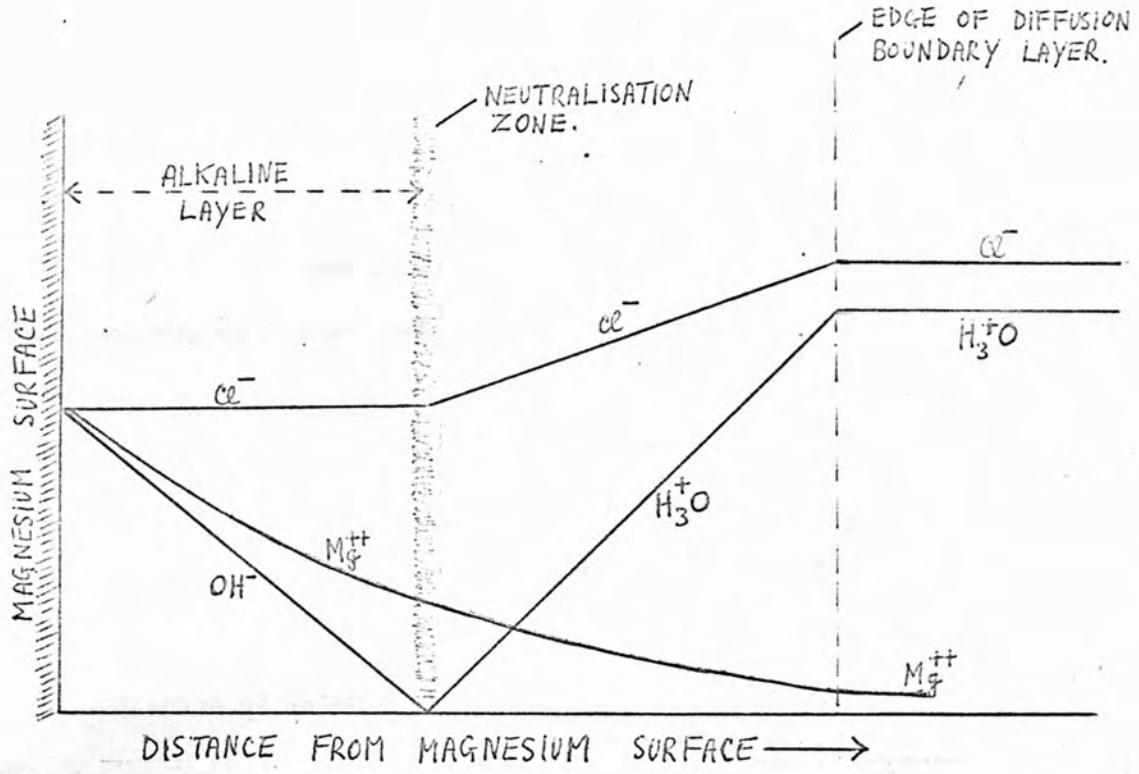

EDGE OF DIFFUSION BOUNDARY LAYER.
NEUTRALISATION ZONE.
ALKALINE LAYER
MAGNESIUM SURFACE
Cl^-
Cl^-
Cl^-
H_3^+O
H_3^+O
Mg^{++}
OH^-
Mg^{++}
DISTANCE FROM MAGNESIUM SURFACE ⟶

Figure 24

towards chemical control. E.A. Moelwyn-Hughes[69] has incorporated I. Langmuir's[99] ideas on adsorption in a theory of the heterogeneous reactions between liquids and solids and, on the basis of this theory, offered an explanation for the difference between the rates of reaction at two lattice planes of the same solid. Furthermore he has suggested that the diffusion of water to the interface may be the rate determining step in some of these reactions, since the concentration of free water at the interface is altered as a consequence of the production of some ions and the destruction of others with different coordination numbers. Indeed, W.J.C. Orr and J.A.V. Butler[100] have shown that the energy of diffusion of water may be about 5,300 cal./mole. The value of 4,170 cal./mole reported in Section II(e) for the energy of activation of the reaction between magnesium and hydrochloric acid may be too low for the diffusion of water molecules to be rate determining in this case.

One can conclude from the present work that reliable methods for obtaining values for the chemical rate constant and for determining the true area exposed to attack are pre-requisites before much further progress can be made.

REFERENCES

1. W. Nernst, Z. Physikal. Chem, 47, 52, (1904)
2. L. Brunner, ibid., 47, 56, (1904)
3. K. Jablczynski and St. Jablonski, ibid., 75, 503, (1911)
4. (a) R.G. Van Name and G. Edga, Amer. J. Sci., 29, 237, (1910); Z. Physikal. Chem., 73, 97, (1910)
   (b) R.G. Van Name and R.S. Bosworth, Amer. J. Sci., 32, 207, (1911);
   (c) R.G. Van Name and D.U. Hill, ibid., 36, 543, (1913)
   (d) R.G. Van Name, ibid., 43, 449, (1917)
5. T. Ericson-Aurén and W.Palmaer, Z. Physikal, Chem., 56, 689, (1906)
6. M. Wildermann, ibid., 66, 445, (1909); Phil. Mag., 18, 538, (1909)
7. E.N. Von Gapon, Z. Elektrochem., 34, 803, (1928)
8. S. Miyamoto, Trans. Faraday Soc., 29, 789, (1933)
9. P.S. Roller, J. Phys. Chem., 39, 221, (1935)
10. E.A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution", 2nd Edition, Clarendon Press, (1947), p. 37.
11. R.G. Van Name and D.U. Hill, Amer. J. Sci., 42, 301, (1916)
12. M. Hochberg and C.V. King, J. Electrochem. Soc., 97, 191, (1950)
13. e.g., (a) L.L. Bircumshaw and A.C. Riddiford, Quart. Revs. (London) 6, 157, (1952)
    (b) C.V. King, Trans. New York Acad. of Sciences, 10, Series 11, (1948)
14. C.V. King and S.S. Brodie, J. Amer. Chem. Soc., 59, 1375, (1937)
15. H.F. Walton, J. Electrochem. Soc., 97, 219, (1950)
16. P.A. Jacquet, Comp. rend. 201, 1473, (1935)
17. A. Brenner, Proc. Amer. Electroplaters Soc., 28, (1941)
18. N. Ibl and R. Muller, Z. Electrochem., 59, 671 (1955)
19. H.J. Antweiler, ibid., 44, 719, (1938)
20. W. Nernst and E.S. Merriam, Z. Physikal Chem., 53, 235, (1905)

21. C.V. King and M. Schack, J. Amer. Chem. Soc., 57, 1212, (1935)

22. R.S. Johnson and H.J. McDonald, ibid., 72, 666, (1950)

23. K. Nagel and T. Renner, Z. Electrochem., 54, 547, (1950)

24. A.C. Riddiford and L.L. Bircumshaw, J. Chem. Soc., 698, (1952)

25. C.V. King and M.M. Braverman, J. Amer. Chem. Soc., 54, 1744, (1932)

26. M. Centnerszwer and W. Zablocki, Z. Physikal Chem., 122, 455, (1926)

27. O.R. Howell, Proc. Roy. Soc., A.104, 134, (1923)

28. A. Fage and H.C.H. Townend, ibid., A 135, 656, (1932)

29. B. Levich, Acta, Physicochim., U.R.S.S., 17, 257, (1942); J. Phys. Chem. U.S.S.R., 18, 335 (1944); Discuss. Faraday Soc., 1, 37, (1947)

30. C.V. King and W.H. Cathcart, J. Amer. Chem. Soc., 59, 63, (1937)

31. A. Eucken, Z. Electrochem., 38, 341, (1932)

32. M. Eisenberg, C.W. Tobias and C.R. Wilke, J. Electrochem Soc., 10, 306, (1954)

33. T. Von Karman, Z. angew. Math. Mech., 1, 244, (1921)

34. W.G. Cochran, Proc. Camb. Phil. Soc., 30, 365, (1934)

35. V.G. Siver and B.N. Kabanov, J. Phys. Chem. U.S.S.R., 22, 53, (1948); ibid., 23, 428, (1949)

36. D.P. Gregory and A.C. Riddiford, J. Chem. Soc., 3756, (1956)

37. V.G. Levich, Annual Rev. Phys. Chem., 18, 153, (1967)

38. C.V. King, In "Symposium on the Surface Chem. of Metals and Semiconductors," held in 1959 at Columbus, Ohio (published in 1960 by John Wiley and Sons Inc., New York)

See also ref. 13(a)

39. M. Kilpatrick and H. Rushton, J. Phys. Chem., 34, 2180, (1930); ibid., 38, 269, (1934)

40. N. Moriguchi, J. Chem. Soc., Japan, 54, 949, (1933)

41. N. Moriguchi, ibid., 55, 749, (1934)

42. F. Hovorka and E. Yeager, J. Acoust. Soc. Am., 25, 443, (1953)

43. F. Hovorka, R. Penn and E. Yeager, ibid., 31, 1372, (1959)

44. W.E. Rowe and W.L. Nyborg, ibid., 37, 1214, (1965)

45. A.A. Baram and O.A. Kokushkin, Zhur. Priklad. Khim., 41, 2013, (1968)

46. e.g. (a) P.L. Westervelt, J. Acoust. Soc. Am., 25, 69, (1953)

(b) W.L. Nyborg, ibid., 25, 68, (1953)

(c) A.M. Ghabrial, and E.G. Richardson, Acustica, 5, 28, (1955)

(d) W. Gartner, J. Acoust. Soc., Am., 26, 977, (1954)

47. E.A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution", 2nd Edition, Clarendon Press, 1947, p. 371.

48. B. Roald and W. Beck, J. Electrochem. Soc., 98, 277, (1951)

49. A.G. Loshkarev, Zhur. Priklad. Khim., 31, 1493, (1958)

50. W.H. Pearlson and J.H. Simons, J. Am. Chem. Soc., 67, 352, (1945)

51. G. Kortüm, W. Vogel and K. Andrussow, **Dissociation** of Organic Acids in Aqueous Solution, Butterworths, (1961)

52. N.Y. Buben and D.A. Frank-Kamenetskü, J. Phys. Chem. U.S.S.R., 20, 225, (1946)

53. G.E. Boyd, A.W. Adamson and L.S. Myers, J. Am. Chem. Soc., 69, 2836, (1947)

54. A.C. Riddiford, J. Phys. Chem., 56, 745, (1952)

55. C.N. Hinshelwood, "The Kinetics of Chemical Change", Clarendon Press, 1945, p. 214

56. A.C. Riddiford and L.L. Bircumshaw, J. Chem. Soc., 598, (1951)

57. C.M. Tu, H. Davis and H.C. Hottel, Ind. Eng. Chem., 26, 749, (1934)

58. M.B. Abramson and C.V. King, J. Am. Chem. Soc., 61, 2290, (1939)

59. A.C. Riddiford, Advances in Electrochemistry and Electrochemical Engineering, Vol. 4, p.47, (1966)

60. D.A. Frank-Kammenetzkü, J. Phys. Chem. U.S.S.R., 13, 756, (1939)

61. M. Centnerszwer and W. Heller, Z. Physikal Chem., 161A, 113, (1932)

62. W. Kaufmann, "Fluid Mechanics" McGraw-Hill Book Co. Inc., 1963

63. H.S. Carslaw, "The Conduction of Heat" MacMillan and Co. 1921, Chapter VII.

64. E.A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution", 2nd Edition, Clarendon Press, 1947, Chapter 12.

65. M. Centnerszwer, Rec. Trav. Chim., 42, 579, (1923)

66. T. L. O'Connor and H.H. Uhlig, J. Phys. Chem., 61, 402, (1957)

67. R. Davis, T. Dewitt and P. Emmett, ibid., 51, 1232, (1947)

68. T.N. Rhodin, J. Am. Chem. Soc., 72, 4343, (1950)

69. E.A. Moelwyn-Hughes, "Physical Chemistry" Pergamon Press, (1957), p.1164

70. E. Wicke, M. Eigen and T. Ackermann, Z. Physikal Chem., N.F.I., 340,(1954)

71. H.D. Beckey, Proc. 4th Int. Cong. Electron Microscopy, Springer, Berlin, (1958)

72. B.E. Conway "Modern Aspects of Electrochemistry" Vol.3, 98, (1964)

73. J.T. Edward, J. Chem. Ed., 47, 261, (1970)

74. J.W. McBain and J.R. Vinograd, J. Am. Chem. Soc., 63, 2008, (1941)

75. V.G. Levich, "Physicochemical Hydrodynamics" Prentice-Hall Inc., (1962)

76. R.A. Robinson and R.H. Stokes "Electrolyte Solutions", Butterworths Sc. Pub.

77. J. Marangozis and A.I. Johnson, Can. J. Chem. Eng. 40, 231, (1962)

78. E.R. Gilliland and T.K. Sherwood, Ind. Eng. Chem., 26, 516, (1934)

79. T.H. Chilton and A.P. Colburn, ibid., 26, 1183, (1934)

80. J.N. Brönsted and K.J. Pedersen, Z. Physikal Chem., 108, 185, (1924)

81. H.S. Taylor, Z. Elektrochem., 20, 201, (1914)

82. R.P. Bell, "The Proton in Chemistry", Methuen and Co. Ltd., (1959), p. 155

83. R.P. Bell and W.C.E. Higginson, Proc. Roy. Soc., A 197, 141, (1949)

84. J.N. Brönsted, Chem. Revs., 5, 322, (1928)

85. F.H. Westheimer, J. Org. Chem., 2, 431, (1938)

86. R.P. Bell, "The Proton in Chemistry" p.160.

87. R.G. Pearson and R.L. Dillon, J. Am. Chem. Soc., 75, 2439 (1953)

88. L.P. Hammett, "Physical Organic Chemistry", New York, (1940), p.261

89. R.P. Bell. Proc. Roy. Soc., A 154, 414, (1936)

90. P.J. Horiuti and M. Polanyi, Acta. Physicochim. U.R.S.S., 2, 505, (1935)

91. R.P. Bell, "The Proton in Chemistry", Chapter X.

92. R.G. Pearson, J. Am. Chem. Soc., 70, 204, (1948)

93. R.P. Bell, M.H. Rand and K.M.A.Wynne-Jones, Trans. Faraday Soc., 52, 1093, (1956)

94. J.J. Weiss, J. Chem. Phys., 41, 1120, (1964)

95. B.E. Conway, J. O'M Bockris and H. Linton, J. Chem. Phys., 24, 834,(1956); G.C. Pimentel and A.L. McClellan, "The Hydrogen Bond", W.H. Freeman and Co., San Fransico, (1960).

96. Discussions of the Faraday Society, "The Kinetics of Proton Transfer Processes", 39, (1965)

97. J. Marangozis, Corrosion, 24, 255, (1968)

98. G.E. Kimball, J. Chem. Phys., 8, 199, (1940)

See also Glasstone, Laidler and Eyring, "Theory of Rate Processes", McGraw-Hill, New York, (1941), Chapter X.

99. I. Langmuir, J. Am. Chem. Soc., 38, 2221, (1916)

100. W.J.C. Orr and J.A.V. Butler, Trans. Chem. Soc., 1273, (1935)

Appendix Setting Out a Method of Obtaining Roller's Solution

The equation $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$, $0 < x < L$ ..... (1)

was solved subject to the following boundary conditions:

$\frac{\partial c}{\partial x} = 0$, when $x = 0$ ..... (2)

and $- D \frac{\partial c}{\partial x} = k_c C$, at $x = L$ ..... (3)

Roller's initial condition was c = constant, at t = 0; but in the general case we set $c = f(x)$, at $t = 0$ ..... (4).

The function $c = e^{-D\alpha^2 t}(A \cos \alpha x + B \sin \alpha x)$ ..... (5),

where A, B and α are constants, satisfies equation (1).

$\therefore \frac{\partial c}{\partial x} = e^{-D\alpha^2 t} (B \alpha \cos \alpha x - A \alpha \sin \alpha x)$ ..... (6).

Making use of equations (2) and (6), we have

$0 = e^{-D\alpha^2 t} . B \alpha$,

$\therefore B = 0.$

Hence a solution of equation (1) is

$c = Ae^{-D\alpha^2 t} . \cos \alpha x$ ..... (7)

However, the general solution of equation (1) is

$c = \sum_{n=1}^{\infty} A_n e^{-D\alpha_n^2 t} . \cos \alpha_n x$ ..... (8)

In order to determine the values of α_n, use is made of the boundary condition expressed by equation (3). Thus from equations (3), (6) and (7), we have $\alpha D \sin \alpha L = k_c \cos \alpha L$,

i.e., $\alpha L \tan \alpha L = k_c L/D$ ..... (9)

The trigonometrical equation (9) can be solved by a graphical method to give the values of α_n for substitution in equation (8).

In order to complete the solution of equation (1), it is necessary to determine the values of A_n. This can be done by the method of Fourier's series. Thus making use of equations (4) and (8) we have

$$f(x) = \sum_{n=1}^{\infty} A_n \cos \alpha_n x \qquad \ldots\ldots (10)$$

Upon multiplying both sides of equation (10) by $\cos \alpha_n x$ and integrating between the limits $x = 0$ and $x = L$, there is obtained

$$\int_0^L (\cos \alpha_n x)\, f(x)\, dx = A_n \int_0^L \cos^2 \alpha_n x.\, dx,$$

$$\text{i.e. } A_n = \frac{\int_0^L f(x).\cos \alpha_n x.\, dx}{\int_0^L \cos^2 \alpha_n x.\, dx} \qquad \ldots\ldots (11)$$

since it can be shown that all the integrals $\int_0^L \cos \alpha_m x.\cos \alpha_n x.dx$ are zero, except when $m = n$.

Now $\int_0^L \cos^2 \alpha_n x.\, dx = \frac{1}{2}\int_0^L (1 + \cos 2\alpha_n x)dx = \frac{L}{2} + \frac{\sin 2\alpha_n L}{4\alpha_n}$

If further we set $f(x) = c_o$, a constant, at $t = 0$, there is finally obtained $A_n = 4 c_o \sin \alpha_n L \,/\, 2 L \alpha_n + \sin 2\alpha_n L$

$$= 4 c_o \sin \beta_n \,/\, 2\beta_n + \sin 2\beta_n \qquad \ldots\ldots (12)$$

where $\beta_n = \alpha_n L$.

Therefore the general solution of equation (1) subject to the stated initial and boundary conditions is

$$c = 4 c_o \sum_{n=1}^{\infty} (\sin \beta_n)\, e^{-D\beta_n^2 . t} \cdot \cos \frac{\beta_n . x}{L} \,/\, 2\beta_n + \sin 2\beta_n \quad \ldots\ldots (13),$$

which is the form given by Roller.